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PILOT PLANT FOR TERTIARY TREATMENT OF WASTEWATER WITH OZONE

Clayton S. Wynn, et al

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Pilot Plant for Tertiary Treatment of Wastewater with Ozone

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The pilot plant used three major process steps: (1) generation of ozone gas from oxygen, including preconditioning of the gas feed and means of recirculating the gas; (2) dissolution of ozone from the oxygen carrier gas into the water; and (3) retention of the ozonated water for a period sufficient for the organic contaminants to be oxidized.

Plant performance for each feed is described in terms of COD reduction characteristics and the effects of pH, ozone concentration, feed pretreatment and initial COD on reaction rate. Data are given for ozone solubility and half-life in pure water and various wastewaters. Bacteria kills are reported. Estimates of capital and operating costs are presented for large plants to treat wastewater with ozone and a procedure is given for optimization of costs for large plants.

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* Wastewater treatment
* Pilot Plants
*Chemical oxygen demand
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Water Treatment
Oxygen
~~Economic~~ Evaluation
Cost ~~Minimization~~ analysis

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PILOT PLANT FOR TERTIARY TREATMENT OF WASTEWATER WITH OZONE

by

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Project #17020 DYC

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ABSTRACT

Tertiary treatment of wastewater with ozone in a nominal 50,000 gal./day pilot plant at Blue Plains, Washington, D.C., is described. Plant feeds (about 10 to 100 ppm COD) were effluents from other pilot processes involving nine different biological and physical treatments of the Blue Plains wastewater. Major COD reductions were realized, and product water was practically free of bacteria and oxygen saturated.

The pilot plant used three major process steps: (1) generation of ozone gas from oxygen, including preconditioning of the gas feed and means of recirculating the gas; (2) dissolution of ozone from the oxygen carrier gas into the water; and (3) retention of the ozonated water for a period sufficient for the organic contaminants to be oxidized.

Plant performance for each feed is described in terms of COD reduction characteristics and the effects of pH, ozone concentration, feed pretreatment and initial COD on reaction rate. Data are given for ozone solubility and half-life in pure water and various wastewaters. Bacteria kills are reported. Estimates of capital and operating costs are presented for large plants to treat wastewater with ozone and a procedure is given for optimization of costs for large plants.

This report was submitted by Airco, Inc., Murray Hill, New Jersey, in fulfillment of Project Number 17020-DYC, Contract 14-12-597, under the sponsorship of the Office of Research and Monitoring of the Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. The Blue Plains wastewaters subjected to nine different combinations of pretreatment were successfully treated in the ozone tertiary treatment pilot plant. Average influent COD values ranged from 13 to 99 mg/l.

2. For domestic wastewaters similar to that at Blue Plains, the relations between feedwater COD, product COD, feedwater pH, reaction time, dissolved ozone concentration, and the quantity of ozone dissolved can be calculated from correlations developed here.

3. Estimated capital and unit operating costs (including maintenance and amortization) for large plants to reduce COD from 40 to 20 mg/l with ozone are:

Plant capacity, mgd	1	10	50
Fixed capital cost, 1000 dollars	500	2,400	9,300
Unit cost, cents/ 1000 gal.	24	12	10

4. Ozone production costs, including gas recycling, vary with plant scale and the concentration of ozone generated. In a plant generating 7500 lb ozone/day, estimates based on pilot plant data (see Figure 56) show the combined equipment amortization and power costs for producing ozone to be 8 to 9¢/lb in the range of 1 to 2-1/2 wt percent ozone in oxygen. A shallow cost minimum is exhibited at about 1.7 wt percent. Above about 2-1/2 wt percent, costs increase rapidly with increasing ozone concentration.

5. Relative ozone consumption, expressed as lb ozone dissolved per lb COD feed, increases exponentially with percent COD removal.

6. For a specified percent COD removal, the relative ozone consumption is practically independent of treatment time, feedwater pH, and the exact nature of feedwater pretreatment. It is simply related to the feedwater COD, as shown by Equation 21 and Figure 31.

7. The rate of COD reduction is increased by increased feedwater pH and by increased dissolved ozone concentration. This relation is described by Equations 23 and 24.

8. There appear to be no technical limits on the COD removal. However, reaction rates become very slow and relative ozone consumptions very high after 50 to 70% removal.

9. Typical ozone tertiary treatment involves handling gas volumes of the same magnitude as the volume of water treated.

10. The gas-liquid mixers used in the pilot plant are most effective at water flow rates greater than nominal capacity and at gas to liquid volumetric ratios of about one. Their performance is summarized by Figure 11.

11. Cocurrent gas-liquid mixers, as used in the pilot plant, cannot dissolve most of the ozone from the gas stream and simultaneously maintain high dissolved ozone concentrations.

12. Improved mixer designs allowing 90% of the ozone to be stripped from the gas, e.g., multistage mixers operated stage-wise in gas-liquid counterflow, could reduce ozone treatment costs perhaps 20%.

13. The solubility of ozone in wastewater is 10% to 30% less than in pure water.

14. The half-life of dissolved ozone in wastewater shows a dependence on the COD concentration (see Figure 39). For wastewater subjected to extended ozone treatment, the half-life is roughly 45 minutes.

15. Water subjected to ozone tertiary treatment is practically free of bacteria.

16. Whether acidic or basic, the pH of the wastewater changes toward neutrality during ozone tertiary treatment.

17. Nitrogenous matter was not removed by ozone treatment. At high pH, much of it was oxidized to nitrate.

18. Turbidity in the feedwater was reduced by ozone treatment.

19. The pilot plant results confirmed the observations concerning the benefits of ozone treatment of wastewater which are outlined in the Introduction.

SECTION II

RECOMMENDATIONS

1. Construct and operate a full-scale demonstration plant for ozone tertiary treatment of wastewater using the technology described in this report.

2. Concurrently, develop improved counter-flow gas-liquid mixer systems which can simultaneously maintain high dissolved ozone concentrations and dissolve a large fraction of the ozone feed.

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SECTION III

INTRODUCTION

Increasing populations and improving standards of living are placing increasing burdens on water resources. The maintenance or improvement in quality of our finite supplies of fresh water and, in the not distant future, the necessity for direct recycling of water in some parts of the country will demand improved technology for the removal of contaminants from wastewater.

The contaminants in wastewater are many and continually varying, and they are not well characterized according to chemical species. Commonly, the level of contamination is described by either a biological oxygen demand (BOD) or a chemical oxygen demand (COD). BOD_5 is a measurement of the oxygen consumption by aerobic microbes feeding on the contaminants during a 5-day incubation. COD is the oxygen equivalent of the oxidation of the contaminants in hot dichromic acid. In general, the COD analysis is quicker and more reproducible than the BOD_5 analysis. For these reasons, COD will be used in this report to characterize the contaminants in wastewater.

Wastewater treatment is usually divided into three stages: primary, the removal of settleable solids; secondary, the removal of readily biodegradable contaminants; and tertiary treatment. Tertiary treatment is generally the further treatment of wastewater after prior treatment has reduced the COD to less than about 60 mg/l and the BOD_5 to less than about 20 mg/l. It may also include the removal of nitrogenous compounds and phosphates.

Tertiary treatment processes include lime (or other chemical) clarification, filtration, activated carbon adsorption, and

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ozone treatment. Ozone, O_3, is a very powerful oxidant which can oxidize most of the oxidizable contaminants in wastewater. It is, however, an unstable material which must be generated at the point of use and in fairly low concentrations.

Ozone has been used for disinfecting drinking water in other countries for many years. And, it has been used to treat some special industrial wastes, notably for removing cyanides and phenols. However, ozone has not been utilized for general wastewater treatment on any large scale.

Several years ago, Airco ran experiments on ozone tertiary treatment of secondary-treated wastewaters. The favorable results led to a pre-pilot, bench-scale experimental program sponsored by the Federal Water Pollution Control Administration.(1)

On the basis of these laboratory investigations, it was established that ozone tertiary treatment potentially offers the following advantages:

(1) There is a major reduction in both BOD and COD. The reduction is accomplished by destroying, not simply separating the organic material; hence, there are no problems of solids handling or concentrated wastes disposal.
(2) There is pronounced reduction of odor, color, turbidity and surfactants.
(3) All bacteria are killed.
(4) Except for oxygen, no residual chemical additives remain in the product water.
(5) The product water has a high dissolved oxygen concentration (DO). Especially, when using pure oxygen to prepare ozone, the DO is generally greater

than the residual BOD or COD. The effect of such effluent on receiving streams would be that of a negative BOD.

Because of these potential advantages of the process, Airco, in contract with EPA, designed, built and operated a 50,000 gal/day pilot plant for ozone tertiary treatment of wastewater at Blue Plains, Washington, D.C.

The objectives of the pilot plant program were to:

1. Establish the effect of scale-up on:
    a) The rate of ozone transfer from the gas phase to the aqueous phase;
    b) The efficiency of ozone in reducing the chemical oxygen demand (COD);
    c) The removal of organic pollutants from a variety of pretreated waste streams.
2. Determine the effect on the ozone process caused by:
    a) Hydraulic and quality changes in the incoming waste stream;
    b) Various clarification procedures used in pretreatment;
    c) Variation in treatment time.
3. Obtain process data for the design of full-scale plants.
4. Establish the economics of the process. Optimize the important process variables, such as ozone feed ratio to each stage of reaction, the number of stages, process residence time, and effluent pretreatment.

This report contains a description of the pilot plant and its operation, the experimental programs, technical results and their correlation, and an economic assessment of large plants for the ozonation of wastewater. Feed waters for the pilot plant were the products of nine different biological and physical treatments of Blue Plains wastewaters.

The tertiary treatment of wastewater with ozone involves three major steps: (1) generation of ozone gas, including preconditioning of the gas feed and means of recirculating the gas; (2) dissolution of ozone from the oxygen carrier gas into the water; and (3) retention of the ozonated water for a period sufficient for the organic contaminants to be oxidized.

The pilot plant contained six 440-gallon reactors arranged in hydraulic series. At the top of each reactor there was a special, injector-type mixer for dissolving ozone from an ozone-oxygen gas stream. Spent gas from the reactors was dried by adsorption on a desiccant under pressure and recycled to the ozone generator. To maintain the desired dissolved ozone concentration in the reactors, the ozone feed to the mixers was adjusted by varying the gas flow and ozone generator power. The range of variables examined in the pilot plant operation is given in Table 1.

Plant performance for each of the nine pretreated feeds is described in terms of COD reduction characteristics. The effects of pH, ozone concentration, feed pretreatment, and initial COD on reaction rate are presented. Data are also included on ammonia nitrogen reactions, turbidity reduction, ozone generator power consumption, and the solubility and half-life of ozone in pure water and various wastewaters. Bacteriological test results from ozonation of the nine different feeds are tabulated. Estimates of capital and operating costs are presented for ozone wastewater treatment plants with design capacities of 1, 10 and 50 mgd. A procedure for optimization of costs for large plants is described and illustrated by an example.

Table 1.

RANGE OF VARIABLES EXAMINED IN OZONE PILOT PLANT

Variable	Minimum	Maximum
Feedwater:		
Flow, gpm	14	56
COD, mg/l	7.0	149
pH	4.9	10.9
Temperature, °F	61	78
Total treatment time, min.	40	188
Lb ozone dissolved/lb COD feed	0.4	5.4
Ozone concentrations		
Gas from generator, wt %	0.85	5.25
Outlet water from reactor, mg/l	nil	9.1
Number mixers operated	2	6
Mixer flow/feedwater flow	0.54	2.75

SECTION IV

PILOT PLANT AND EQUIPMENT DESCRIPTION

Plant Location

The pilot plant is located at the Blue Plains wastewater treatment plant in Washington, D.C., a large plant serving the Washington metropolitan area. The wastewater to this plant is nearly all domestic waste and has a fairly low level of COD and BOD. An important advantage of this location is the presence of a complex of pilot scale, advanced wastewater treatment processes operated cooperatively by the Environmental Protection Agency and the District of Columbia. These facilities made possible a variety of different wastewater feeds to the ozone treatment pilot plant.

Pilot Plant

A schematic flow diagram of the pilot plant is shown in Figure 1, and a layout of the major equipment is shown in Figure 2. Nominal design capacity of the plant is 35 gpm (50,000 gal/day) of a wastewater feed having a COD level of 40-60 mg/liter. The nominal treatment time of wastewater with ozone is about 1-1/3 hours. Pumps and control equipment are sized to permit plant operations at rates up to 70 gpm.

Wastewater enters the plant through a neutralization tank which has provisions for automatic adjustment of pH by a carbon dioxide sparge system. Dissolved gases, mostly nitrogen, are removed in a spray type, vacuum deaerator operating at about 28 inch Hg vacuum. The water then flows through a series of six 440 gal reactors, each 20 ft high x 2 ft in diameter, in which the actual ozone treatment takes place. Finally, the treated water is detained in a 2000 gal holding tank to permit the residual dissolved ozone to decompose

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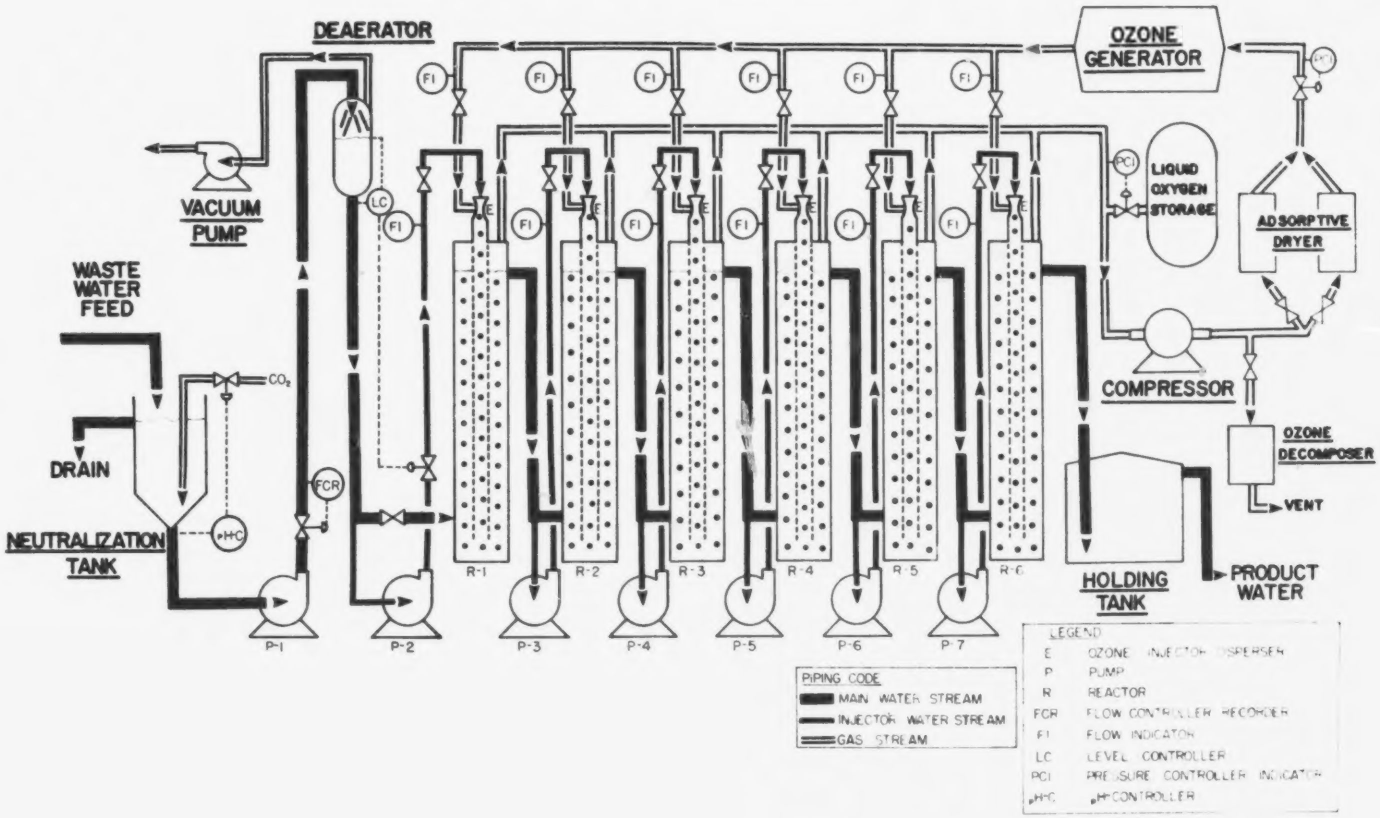
DEAERATOR
OZONE GENERATOR
VACUUM PUMP
WASTE WATER FEED
CO2
DRAIN
NEUTRALIZATION TANK
FCR
pH-C
LC
FI
PCI
E
LIQUID OXYGEN STORAGE
ADSORPTIVE DRYER
COMPRESSOR
OZONE DECOMPOSER
VENT
HOLDING TANK
PRODUCT WATER
R-1
R-2
R-3
R-4
R-5
R-6
P-1
P-2
P-3
P-4
P-5
P-6
P-7
PIPING CODE
MAIN WATER STREAM
INJECTOR WATER STREAM
GAS STREAM
LEGEND
E OZONE INJECTOR DISPERSER
P PUMP
R REACTOR
FCR FLOW CONTROLLER RECORDER
FI FLOW INDICATOR
LC LEVEL CONTROLLER
PCI PRESSURE CONTROLLER INDICATOR
pH-C pH-CONTROLLER

Figure 1. FLOW DIAGRAM OF PILOT PLANT

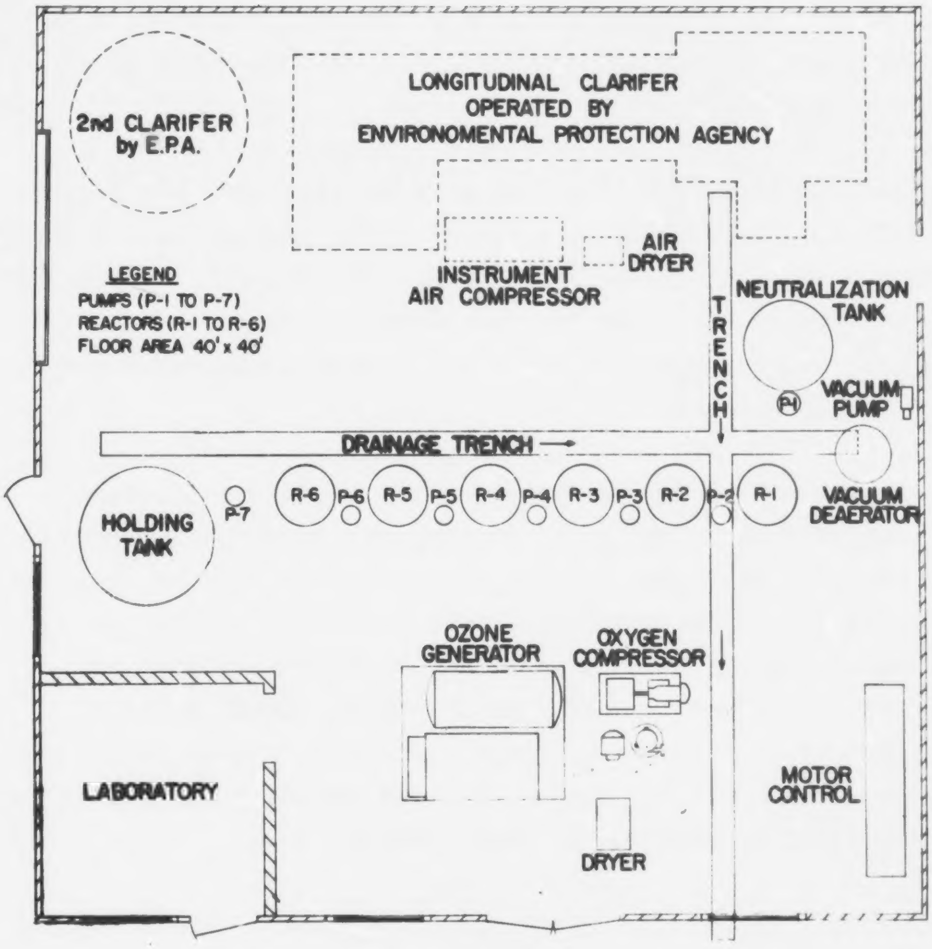
2nd CLARIFER
by E.P.A.
LONGITUDINAL CLARIFER
OPERATED BY
ENVIRONOMENTAL PROTECTION AGENCY
AIR
DRYER
INSTRUMENT
AIR COMPRESSOR
LEGEND
PUMPS (P-1 TO P-7)
REACTORS (R-1 TO R-6)
FLOOR AREA 40' x 40'
NEUTRALIZATION
TANK
TRENCH
P-1
VACUUM
PUMP
DRAINAGE TRENCH →
HOLDING
TANK
P-7
R-6
P-6
R-5
P-5
R-4
P-4
R-3
P-3
R-2
P-2
R-1
VACUUM
DEAERATOR
OZONE
GENERATOR
OXYGEN
COMPRESSOR
LABORATORY
MOTOR
CONTROL
DRYER

Figure 2. EQUIPMENT LAYOUT OF PILOT PLANT

before it is discharged from the plant. Part of the treated wastewater from the holding tank was used as cooling water for the ozone generator and as seal water for the recycle gas compressor and deaerator vacuum pump.

Ozone is produced from oxygen by electrical discharge in a commercial ozone generator having a nominal capacity of 60 pounds per day.

Pure oxygen, rather than air, is used as the feed gas to the ozonator in order to realize greater power efficiency in the generation. In addition, ozone generators require a very dry gas for maximum efficiency and low maintenance. The use of pure oxygen, rather than air, greatly reduces the volume of gas that must be dried.

Although pure oxygen is not very expensive in large quantities, its cost, together with the limited concentrations of ozone (1%-4% by wt) that can be produced efficiently by existing types of ozone generators, makes recycling of the oxygen an economic necessity. The deaeration of the wastewater feed to the plant prevents the build-up of inert gases in the gas cycle. In the pilot plant, the gas recycle stream usually was 90-95 vol % oxygen, the remainder being nitrogen and carbon dioxide roughly in the ratio of 2:1.

The gas cycle through the plant is as follows: Gas from the ozone generator, consisting of an ozone in oxygen mixture, is fed in parallel to the dissolving equipment of the six reactors. The spent gas is collected from the reactors in parallel, compressed to about 50 psig in a Nash water ring compressor, and dried to a dew point of -60°F in an adsorption dryer which is automatically regenerated by low pressure purge. The spent gas from the reactors contained some residual ozone, but most of it was lost through decomposition in the dryer and by dissolution in the seal water of the compressor. Make-up oxygen from liquid storage tanks was automatically fed to the suction side of the compressor as required to maintain a constant suction pressure. The consumption of make-up oxygen was measured by a positive displacement gas meter.

Emergency gas vent lines and vents from the gas sampling system passed through an electrically heated furnace operating at 320°C. This assured the decomposition of any residual ozone before discharge of the gas to the atmosphere.

The operating characteristics of the major pieces of pilot plant equipment are described below, and the equipment specifications are outlined in Appendix 2.

Materials of Construction

The neutralizing tank, deaerator, and reactors are made of mild steel. The inside surfaces of the reactors have a hot-applied, coal-tar bitumastic lining, and the inside of the vacuum deaerator tank is coated with a baked epoxy coating. Pipes carrying dry gas are aluminum (Spec. 6061-T-6), and those carrying the wet, spent gas are type 316 stainless steel. Water piping and mixers are of polyvinyl chloride (PVC), Type I. All wetted parts of pumps and the compressor are made of stainless steel (type 316). Pipe flanges are sealed with Teflon enveloped asbestos gaskets, and fluorinated elastomers are used for shaft seals. Throughout the test period, no corrosion of these components was evident.

Originally, the mild steel holding tank was lined with an epoxy-bonded enamel. This coating was attacked very severely by the ozone and, after two months use, the residual coating was removed by sandblasting and a solvent coal-tar bitumastic coating was applied. This coating showed some evidence of blistering in the gas space after six months of service.

Appendix 3 contains additional corrosion test results for several common metals of potential usefulness in equipment fabrication.

Post-Ozonation Apparatus

The apparatus shown in Figure 3 was used to gather additional process data. Product water from the pilot plant is placed in a 3-liter flask and subjected to an ozone sparge for an additional 4-8 hours in order to carry the ozone treatment nearly to completion. The gas sparge is then stopped; contemporaneously, the liquid and gas are analyzed for ozone concentration, and a sample for COD analysis is taken. Subsequently, several analyses of the dissolved ozone (DO_3) are made over a 40 to 60 minute period.

The COD value affords a point on the reaction curve near the reaction end point. From the contemporaneous gas and liquid analyses, ozone solubility in the wastewater can be calculated. By plotting the log of dissolved ozone concentration against time, as is shown in the bottom of Figure 3, the rate of ozone decomposition in the wastewater (assuming first order kinetics) can be obtained.

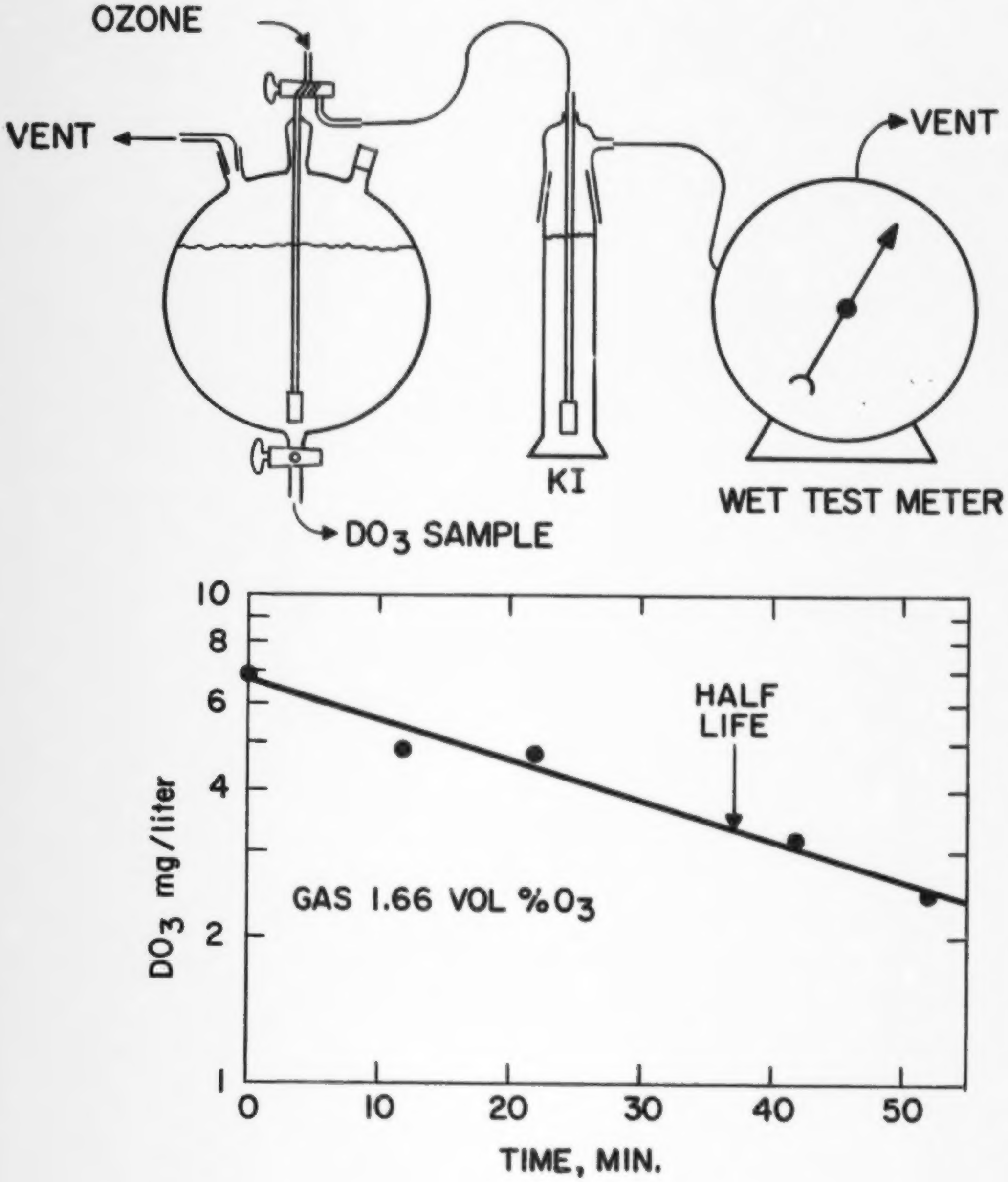
OZONE
VENT
VENT
KI
WET TEST METER
DO$_3$ SAMPLE
10
8
6
4
2
1
DO$_3$ mg/liter
HALF LIFE
GAS 1.66 VOL %O$_3$
0
10
20
30
40
50
TIME, MIN.

Figure 3. POST-OZONATION APPARATUS

SECTION V

PILOT PLANT OPERATION

General

After a several week start-up period, routine pilot plant operations on wastewater were started on February 1, 1971 and continued to September 30, 1971 with only minor interruptions (caused mostly by equipment failure and process upsets in the upstream pretreatment processes). The ozone pilot plant was normally operated twenty-four hours per day, five days per week. It was staffed by three operators, one for each shift, a chemical analyst, and a senior research engineer.

During most of the operations, wastewater was piped into the neutralizing tank from the upstream pretreatment processes. The desired plant feed flow was pumped from there into the vacuum deaerator, and the excess wastewater overflowed from the neutralizing tank to drain. The lime clarified secondary effluent from the main Blue Plains plant was pumped into the deaerator directly from the longitudinal clarifier system location in the ozone pilot plant building (see Figure 2). The available flows for several of the feeds examined were less than the 35 gpm nominal capacity of the pilot plant. The plant was operated both in a constant flow mode and in a variable flow mode in which the flow approximated the diurnal flow to the Blue Plains plant.

Adjustment of pH in the neutralizing tank was accomplished by using carbon dioxide. A small quantity of air was continuously sparged into the tank to keep it stirred. Carbon dioxide was automatically introduced into the air stream as required to maintain a constant pH.

The pilot plant incorporated only a few automatic controls;

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these were; feedwater flow rate, feedwater pH, water level in the vacuum deaerator, make-up oxygen flow, and compressor outlet pressure. All other plant parameters were controlled manually. Water flow and gas flow to each mixer were indicated by glass rotameters and were controlled by hand-operated valves. Pressures of gas and liquid streams were measured with bourdon gauges. The ozone feed was adjusted by manually varying both the gas flow rate and electric power input to the ozone generator. Coarse adjustment of ozone feed was made in proportion to feedwater flow rate, and fine adjustment was made to maintain the desired dissolved ozone concentration in the overflow from each reactor. For the most part, manual analyses of dissolved ozone were used as the control basis, but as is mentioned in the discussion of analytical methods, below, a "bread-board" continuous dissolved ozone analyzer was used for this purpose for a period of several weeks.

The pilot plant responded very rapidly to changes in operating parameters. It could be started up in less than 20 minutes and shut down in less than 10 minutes. Because of the rapid response to changes, composite sampling of the water and gas streams was not necessary.

A number of parameteric studies were made on the various pilot plant feeds. These include studies of the effects of feedwater pH, treatment time, ozone dosage, number and sequence of mixers operated, and ozone distribution to the mixers. The nature of these studies is evident from the data listings in Appendix 6. In many of these studies, advantage was taken of the rapid plant response by "interleaving" the parameteric changes. In examining the effects of several values of pH, for example, instead of making several runs at one pH, then several at the next pH, and so on, the pH was changed every shift until four to six sets of data were obtained for each pH value. Thereby, the average data for each of the several pH values similarly reflected any possible long term drifts in the feedwater characteristics.

Safety

Ozone treatment of wastewater involves the handling of two potentially dangerous substances: ozone and pure oxygen. Ozone is toxic, and oxygen can increase fire hazards. However, with moderate precautions, both materials can be handled with complete safety. A copy of the safety rules and procedures employed in the pilot plant is shown in Appendix 4. With these procedures, no accidents or hazardous situations associated with oxygen or ozone were experienced during the more than nine months of pilot plant operation.

An oft quoted measure of the toxicity of gases is the Threshold Limit Values (TLV) set by the American Conference of Governmental Industrial Hygienists which "represents conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect".(2) The TLV of ozone in air is 0.1 parts per million by volume (ppmv). However, ozone has a very strong, pungent odor. The minimum concentration detectable by odor is only about 0.02 ppmv, and at the TLV concentration, the odor is very strong and irritating. This makes it unlikely that anyone would voluntarily remain in dangerously high ozone concentrations.

The degree of possible hazards from ozone can be placed in perspective by comparison with chlorine, a material used routinely in wastewater treatment.(3) Chlorine is considered to be less toxic than ozone, the tentative TLV being 1 ppmv. However, the minimum concentration of chlorine detectable by odor is about 3 ppmv. Thus, the TLV of ozone is much greater than the concentration detectable by odor, while the converse is true for chlorine. Moreover, no large quantities of ozone would ever be accumulated in a wastewater treatment plant; being unstable, it is generated only as needed, and then only in low concentrations. And in the event of system leaks, ozone generators can be shut down instantaneously. Chlorine, on the other hand, is commonly transported and stored in large quantities as liquid under considerable pressure; any catastrophic leak in such a chlorine system can release large quantities of concentrated chlorine, thereby creating a major hazard. Thus, it appears that even though ozone is more toxic than chlorine, in the practical applications to wastewater treatment ozone should be judged less hazardous than chlorine.

It may be mentioned that high concentrations of ozone are very unstable and can decompose with explosive violence. But under no known circumstances can such high ozone concentrations be produced in conventional electric ozone generators.

Pure oxygen is not toxic; twenty percent of normal air is oxygen. But high concentrations of oxygen grossly enhance the ease of ignition and flame temperature of any combustible substance. High concentrations of oxygen cannot be detected by the physical senses—odor, taste, or color—and for this reason, possibly hazardous situations are not always immediately obvious. Thus, oxygen may present a more insidious hazard than ozone. However, very large quantities of pure oxygen are handled daily for industrial and medical purposes with virtually no accidents. Proper safety procedures are simple and well established; a minimum of combustible materials and possible ignition sources are allowed in the vicinity of pure oxygen systems, and the areas must be well ventilated.

The ozone in oxygen treatment of wastewater does introduce two particular, if somewhat remote, hazards. First, combustible materials, e.g., oils and greases, must be removed from the wastewater before ozone treatment. If there is any practical possibility that such materials could pass through the upstream treatment processes, reliable means for detection of combustibles must be incorporated at the inlet of the ozone treatment plant with provisions for automatic plant shut-down. The second possible hazard is more remote, involving the high dissolved oxygen concentrations in the product water. The partial pressure of oxygen in the product water is about five times that in air. Oxygen will tend to desorb from the water into the air. In the rare combination of (a) a large body of undiluted, oxygen saturated product water, (b) no wind, and (c) a strong atmospheric temperature inversion, oxygen enriched air could accumulate and create a flammability hazard. This rather unlikely hazard can be completely removed by arranging the plant outfall so that the product water is rapidly mixed with the receiving waters.

Data Collection

Wastewater sampling taps are located at the outlets of the neutralizing tank and vacuum deaerator, in the water overflow and recycle lines of each of the six reactors, and at the outlet of the product holding tank. Samples were routinely collected from these taps, and if the sample had been exposed to ozone, any residual dissolved ozone was removed by an inert gas sparge.

Gas sampling taps are located at the outlets of the ozone generator, the compressor and the dryer, and in the gas return lines from each reactor. These sampling taps were connected by metal tubing to a valve manifold in the laboratory where the various gas samples were analyzed for ozone concentration.

Plant operating parameters were monitored continously, and once each eight-hour shift a completed set of plant data was obtained. These data were collected according to a schedule based on the feedwater flow rate so that the data collection followed the flow of a single slug of water through the treatment process. Data collected included:

1. All gas and liquid flows and pressures.
2. The COD as the water slug leaves each reactor.
3. The ozone concentration in the gas from the ozone generator and in the spent gas from each reactor.
4. The pH, temperature and turbidity of the feed and product water.
5. The dissolved ozone concentration in the water in each reactor.
6. The ozone generator power parameters.
7. Make-up oxygen meter readings.

The operating parameters were recorded on log sheets; the analytical results were recorded in notebooks; and the pertinent information from these basic sources was then recorded on "Reactor Profile Data Sheets" for later computer reduction of the data. A copy of the data form is shown in Appendix 6, together with a summary listing of the 296 complete sets of plant data collected during operations.

In addition to the complete plant data sets, other wastewater samples were collected from the pilot plant at less frequent intervals. These were subjected to additional analyses which included bacteriological assay by an independent commercial laboratory and analyses for BOD_5, TOC, and total Kjeldahl, ammonia, nitrite, and nitrate nitrogen concentrations by the EPA analytical group at Blue Plains.

Analytical Procedures

General. The analytical procedures used in the pilot plant work are described in detail in Appendix 5. Most of the analytical methods employed were either standard procedures$^{(4,5)}$ or slight modifications thereof.

COD Analyses. For reasons mentioned in the introduction and in Appendix 5, COD was selected as the method of characterizing the contaminants in wastewater. Since the investigation of COD reduction during ozone treatment was a primary objective of this work, and because many of the COD levels encountered were very low, much effort was devoted to obtaining accurate and precise COD data.

As finally evolved, the low level COD analytical method described by EPA$^{(4)}$ was used with one modification. Instead of adding mercuric sulfate to each reflux flask as the powder, it was dissolved into the acidified standard potassium dichromate solution beforehand. This was necessary because traces of solid organic contaminants were found in many batches of reagent grade mercuric sulfate. If added to each analytical flask as the solid powder, each flask would receive varying quantities of the heterogeneously distributed contaminant, a situation which could not be corrected from the blank analysis run with each batch of COD samples. It was also found that the quality of the distilled water was critical at low COD values. The use of bottled, pyrogen-free distilled water enhanced the precision of the analyses.

The collection and handling of the COD samples required great care. Only a tiny speck of organic dirt accidentally introduced into the sample produces large errors in the very low range COD analyses. All the samples were collected in glass bottles which had been cleaned with chromic acid solution and well rinsed with good distilled water. The samples were stabilized with reagent grade sulfuric acid during collection and were then immediately sparged with helium gas to remove any residual dissolved ozone.

From the results of replicate analyses, and from the consistency of the COD data obtained from the various reactors (described below), the low range COD determinations (about 5 to 30 mg/l) are believed to be precise within about 1 mg/l.

BOD and TOC. During the latter part of the pilot plant studies, a number of additional water samples were collected, and these were submitted to the EPA analytical group at Blue Plains for BOD_5, total organic carbon (TOC), and nitrogen analyses. (The samples for BOD analysis were not acid stabilized but were refrigerated, and the analyses were started on the same day as collected.)

A comparison of the BOD_5 analyses with the plant COD analyses is shown in Figure 4. (See Table 2 for explanation of effluent abbreviations.) A similar comparison with the TOC analyses is shown in Figure 5. The correlations are not very good, a matter further discussed in Appendix 5.

Dissolved Ozone. The acidic KI method of determining dissolved ozone concentrations used in the prepilot work(1) was used unchanged during the first part of the pilot plant work. But in late June, no feed to the plant was available for several days, and a series of runs on tap water were begun to gather additional data on mixer performance. With the ozone consumption by chemical reaction no longer a masking factor, it was found that an ozone mass balance around individual reactors could not be completed. This eventually led to the conclusion that the acidic KI procedure leads to erratic and usually high results.

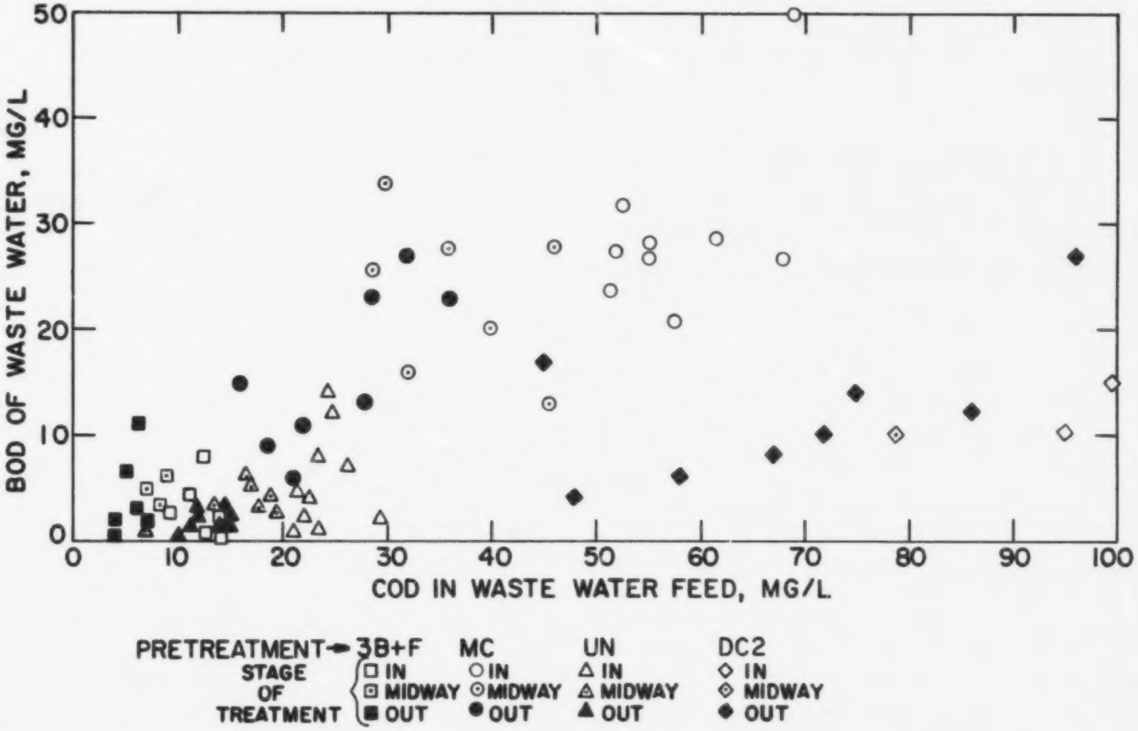

Figure 4. RELATION BETWEEN COD AND BOD IN OZONE-TREATED WATER

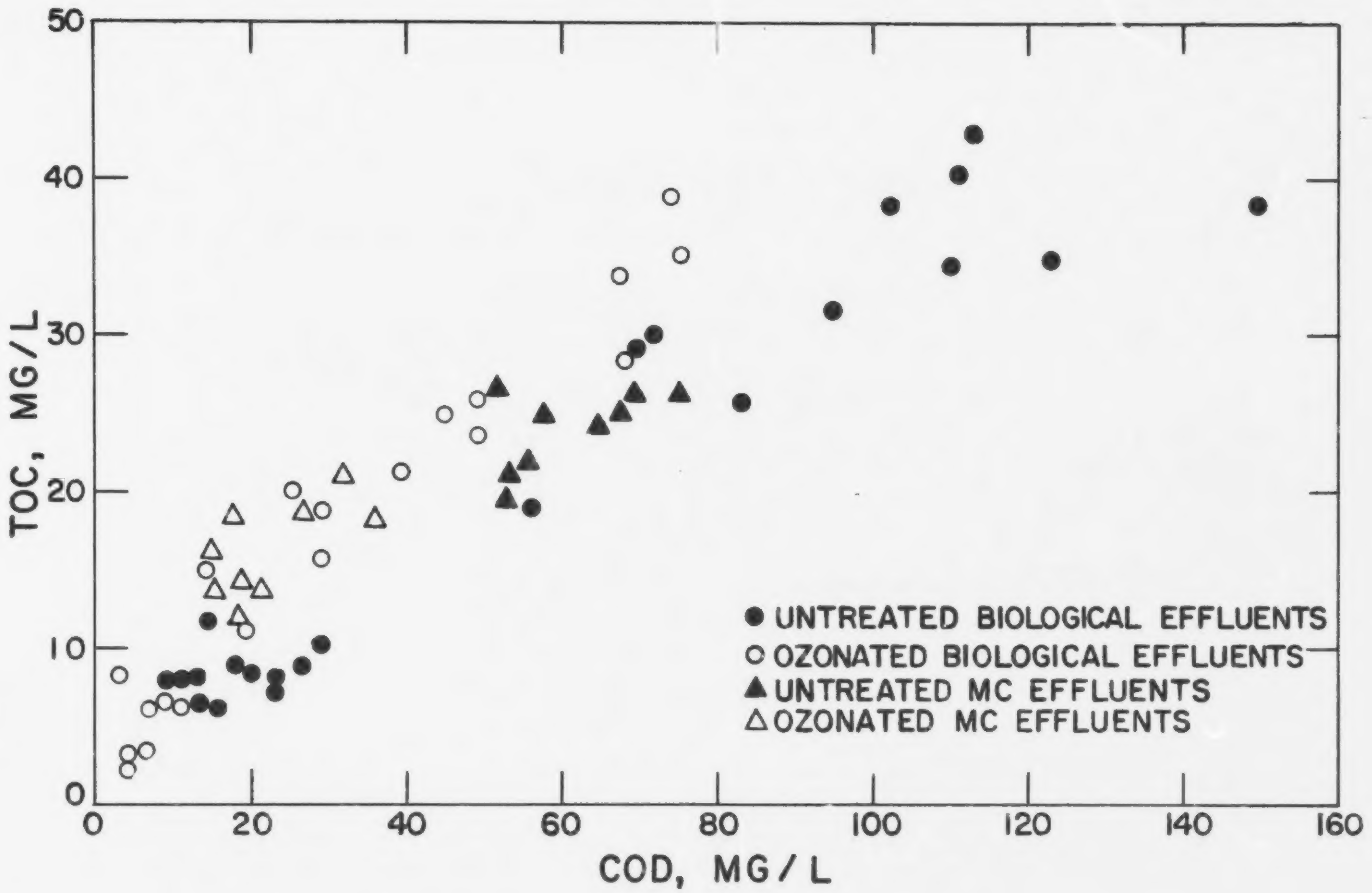

Figure 5. RELATION BETWEEN TOC AND COD IN OZONE TREATED WATER

The alkaline KI method(6) described in Appendix 5 was adopted on June 24, 1971 and used for all subsequent analyses. This method was found to be in generally good agreement with the more cumbersome sparging procedure described in Standard Methods.(5)

The errors in the earlier dissolved ozone analyses do not enter into calculations for ozone consumption since such calculations are based on an ozone gas balance. But the earlier erratic analyses were judged to be too suspect for use in mass transfer and reaction rate correlations and, therefore, (as described later) were not used for these purposes.

Ozone in Gas. The analysis for ozone concentrations in various gas streams was based on the standard potassium iodide method without modification. A description of this procedure is given in Appendix 5.

Continuous Dissolved Ozone Analyses. A simple dissolved ozone analyzer was devised and used to a limited extent for plant control. A sample wastewater stream containing dissolved ozone was passed through a special metering valve which diverted a small fixed flow from the stream into a sparge chamber. The diverted portion was sparged with a large, measured flow of clean air. Ozone in the air stream was determined by a commercial ozone detector. The meter reading was proportional to the dissolved ozone concentration in the water sample.

This relatively simple device operated satisfactorily on well-filtered plant feeds and demonstrated the feasibility of continuously controlling ozone dosage on the basis of dissolved ozone levels. However, even small quantities of suspended matter in the water were found to repeatedly plug the metering valve. We believe that a refined device of this type, or probably any of the several available dissolved chlorine analyzers using the iodometric methodology, could be used in a large plant to continuously measure dissolved ozone levels for control purposes.

SECTION VI

SOURCES OF FEEDWATER

Available Pretreatments

The Blue Plains Water Pollution Control Plant, the location of the ozone pilot plant, is a very large (225 Mgd) facility serving the Washington, D.C. metropolitan area. Treatment consists of primary clarification, activated sludge secondary treatment, and chlorine disinfection. The wastewater is nearly all domestic waste and, therefore, has a fairly low BOD_5 (about 130 mg/l) and COD (about 300 mg/l).

In addition to providing a source of fairly typical domestic wastewater, a great virtue of the location is the presence of a complex of pilot scale (50,000 to 200,000 gpd) advanced wastewater treatment processes operated cooperatively by the Environmental Protection Agency and the District of Columbia. These facilities afforded a large variety of secondary and tertiary pretreatments of the feedwater to the ozone pilot plant. The pretreatments available are described below, together with the abbreviations assigned to each.

Each of the EPA/DC pilot processes has been described elsewhere.(7,8,9) Since several of them can be operated in various modes, only a brief description of the processes as they were used to feed the ozone pilot plant will be given here.

3B - The three-stage biological process(7) used three biological processes for removing both carbonaceous and nitrogenous materials. It consists of (1) a more or less conventional, high rate, activated sludge plus clarification step for removal of carbonaceous materials, followed by (2) an aerobic sludge plus clarification step for converting nitrogenous material to nitrate, followed by (3) an anaerobic sludge plus clarification step for reducing nitrates to nitrogen gas. In order to supply carbonaceous nutrients for the denitrifying organisms, carefully controlled quantities of methanol are added during the third step.

UN - The Unox(9) process is a Union Carbide multi-stage activated sludge process in which dissolved oxygen is supplied from pure oxygen gas instead of air. High BOD reduction rates are realized by operating with high concentrations of mixed liquor biological solids. The pilot unit consisted of four stages in series, each equipped with submerged turbine type oxygen dissolution equipment.

MC - In the two-step mineral clarification process(7), raw wastewater was first gravity clarified with comparatively high concentrations of lime, and then it was further gravity clarified with ferric salts in a second unit.

L - Lime clarification is also useful as a tertiary treatment for removing both phosphates and suspended solids. In the pilot unit, effluent from one of the secondary biological processes was gravity clarified with comparatively small concentrations of lime. The clarified overflow was carbonated with CO_2 to a specified pH (8 to 10.5), then reclarified.

F - The pilot filtration unit removed suspended solids by gravity filtration through a dual media bed of granular anthracite atop sand.

C - The carbon adsorption pilot unit consisted of five activated carbon columns operating in series, in which the carbon was regularly back-washed and periodically replaced. Both residual suspended solids and dissolved organic matter were removed.

CL - The break-point chlorination pilot process oxidized dissolved ammonia in secondary effluents to nitrogen gas by the carefully controlled addition of chlorine. The "break-point" is reached when the ammonia concentration is reduced to zero, free available chlorine is detected, and the total residual chlorine is minimized. Good mixing, pH control, and chlorine dosage control are required to minimize undesirable byproducts.

DC2 - In addition to the wastewaters pretreated in the pilot processes, secondary effluent from the main plant was available for feed to the ozone pilot plant. A stream was pumped from the secondary clarifiers before chlorine disinfection.

Feedwater Treated

Wastewaters subjected to nine combinations of pretreatment were examined in the ozone pilot plant. A summary of these nine pretreatments, together with the symbols used to designate each one throughout this report, are listed in Table 2.

The periods during which each feed was examined are listed in Table 3. Also shown are the arithmetic average COD's of each feed during the period. Feed COD's range from those of a marginally treated secondary effluent to those so well pretreated that ozone treatment is only a final polishing and disinfection step. The period that each feed was examined was determined by availability from upstream processes and the extent of parametric studies planned.

Table 2.

PRETREATMENT OF WASTEWATER FEED TO PILOT PLANT

DESCRIPTIVE SUMMARY

I. EPA/District of Columbia Pilot Plants

Process Abbreviation	Processing Scheme
3B + F	A 3-stage biological treatment consisting of high rate activated sludge, aerobic nitrification, and anaerobic denitrification, plus dual media filtration.
3B + L + F	3-stage biological treatment plus lime clarification plus dual media filtration.
UN or UNOX	Oxygen activated sludge.
UN + L + F	Oxygen activated sludge plus lime clarification plus dual media filtration.
MC	Lime and mineral clarified raw wastewater.
MC + CL	Lime and mineral clarified waste water plus break-point chlorination.
MC + CL + C	MC + CL plus activated carbon adsorption.

II. Blue Plains Plant Effluent

DC2	Secondary effluent from District of Columbia Water Pollution Control Plant.
DC2 + L	DC2 effluent plus lime clarification.

Table 3.

INDEX OF FEEDWATERS TREATED IN PILOT PLANT

Pretreatment	Average COD	Date
3B + F	13.5	8/27-9/12/71
3B + L + F	25.9	2/1-5/7/71
UN	26.1	8/2-8/18/71
UN + L + F	16.9	5/10-5/20/71
MC	53.7	7/12-7/30/71
MC + CL	46.6	8/20-8/27/71
MC + CL + C	14.7	5/21-7/9/71
DC2	98.9	9/13-9/23/71
DC2 + L	72.4	9/24-9/30/71

Feedwater Characteristics

COD frequency distribution charts are shown in Figures 6, 7 and 8 for the nine feeds to the ozone pilot plant.

The points for the moderate and high COD feeds shown in Figure 6 (log COD vs probit) generally fall along a straight line showing that the percentage variation in COD about the mean is normally (Gaussean) distributed. For the lower COD feeds shown in Figure 7 (COD vs probit), the straight line fall of the data indicates that the COD values (rather than percentage deviation) are normally distributed about the mean. On can easily suspect, however, that this reflects the normal error in COD analyses at the low COD levels, and that the percentage variation is normally distributed for all of the feeds.

The 3B + L + F feed is the exceptional case, as is shown in Figure 8. About half the data show a normal distribution at a low COD, typical of the other feeds subjected to 3B pretreatment. The other half, however, show a non-normal distribution at a much higher COD level. This was due to excess methanol resulting from poor control of the methanol addition to the denitrification stage of the 3B process during the early period of its operation. This also accounts for the fact that the average COD shown for this feed in Table 3 is higher than that for the less thoroughly pretreated 3B + F feed. The 3B + L + F feed exhibited one other anomaly. On at least two occasions, some substance appeared which liberated iodine from acidic KI solution. The exact identity of this substance is not certainly known, but a nitrosamine is suspected. In any event, it appeared to be destroyed in the first stage of ozone treatment.

The suspended solids content (as reflected by turbidity) of

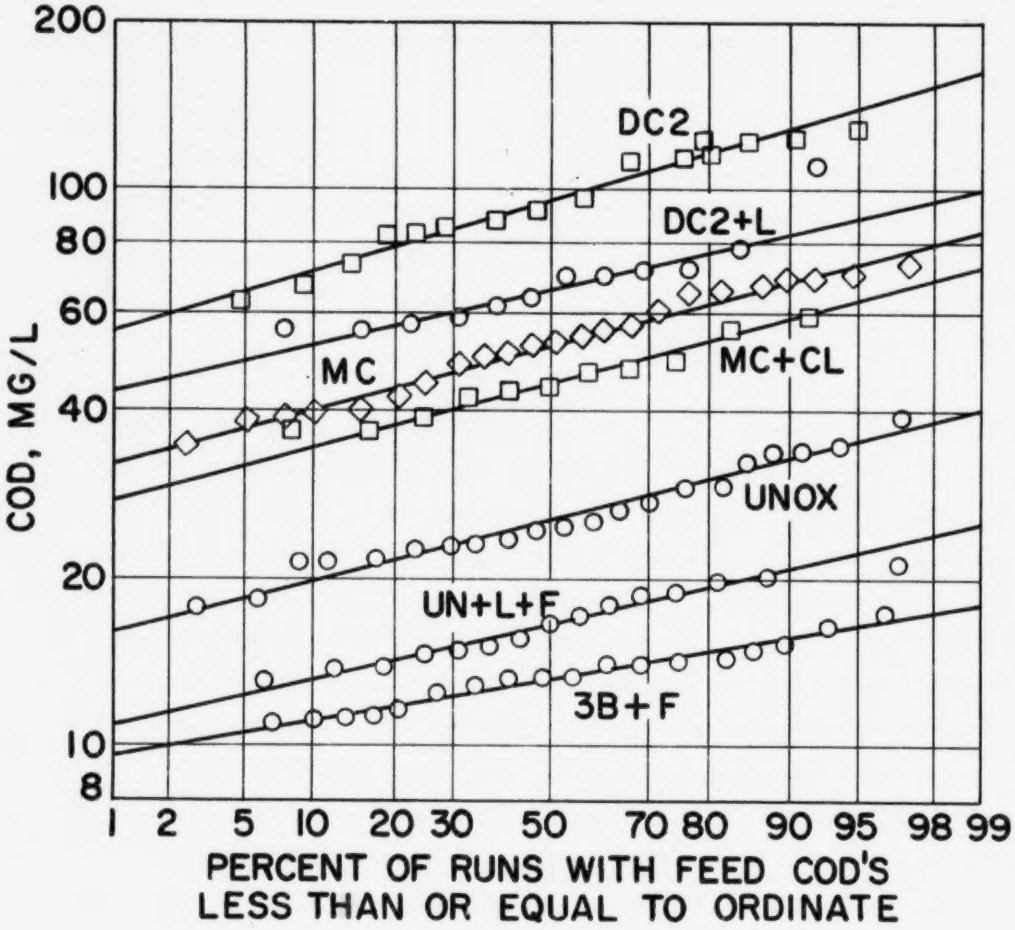

Figure 6. DISTRIBUTION CURVES FOR HIGH COD FEEDS

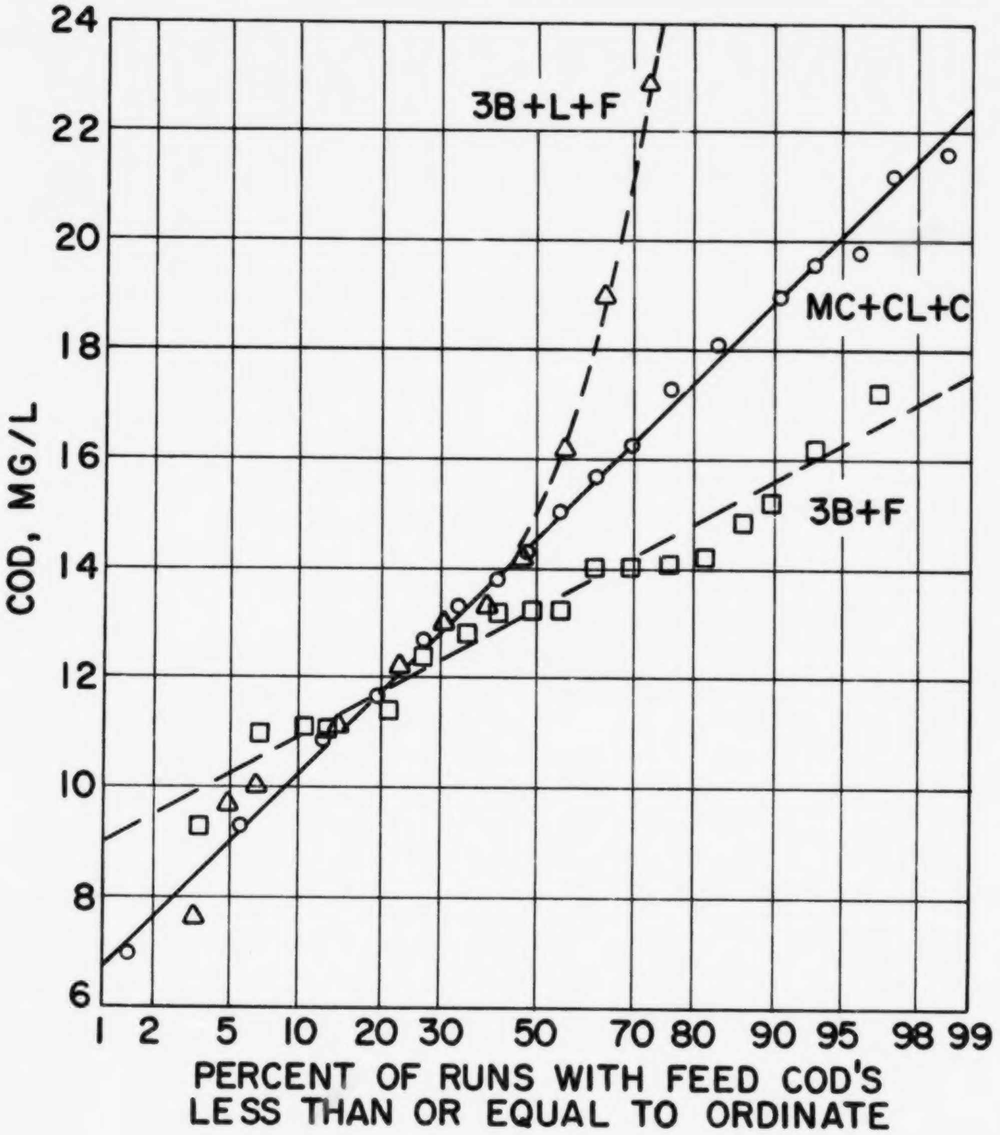

Figure 7. DISTRIBUTION CURVES FOR LOW COD FEEDS

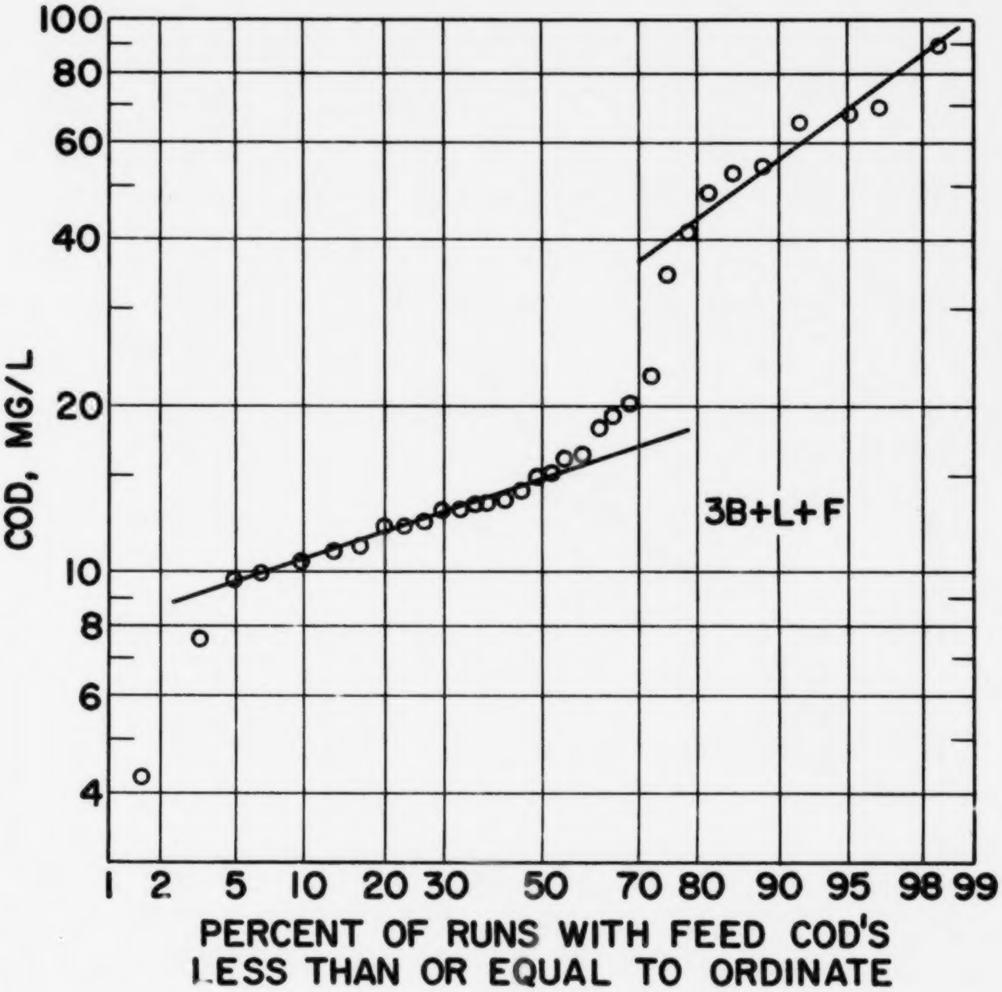

Figure 8. DISTRIBUTION CURVES FOR 3B + L + F FEED

the feeds varied according to the degree of pretreatment. Feed turbidities are discussed below in sections dealing with turbidity reduction.

The MC, MC + CL, DC2, and DC2 + L feeds contained a quantity of surfactants sufficient to cause minor frothing problems in the first stage of the ozone pilot plant. However, the ozone dose in the first stage alone was enough to eliminate the frothing problem in subsequent stages.

The feeds pretreated by the 3B and CL processes (3B + F, 3B + L + F, MC + CL, MC + CL + C) contained very little ammonia nitrogen. The other feeds contained ammonia in varying degrees. The latter are described in the discussion of nitrification by ozone treatment, below.

The only modification of the feeds to the ozone pilot plant was pH adjustment, generally using only carbon dioxide to lower the pH. For the MC + CL + C feed, however, it was desired to operate at pH values higher than that of the feed. In this one case, the pH was raised to a preset value by a constant rate addition of sodium hydroxide solution combined with automatically controlled carbon dioxide sparging.

A major objective in treating the MC + CL pretreated feed was to determine the removal of residual chloramines and the effects of available chlorine on the ozone process. The data obtained were not as reliable as those for the other feeds. First, the upstream CL pilot equipment began malfunctioning just about as soon as the feed was introduced into the ozone plant. Second, attempts to analyze for chloramines and available chlorine in the presence of dissolved ozone produced erratic results. Analyses were made with KI on samples before and after sparging with helium to strip out the ozone.

Often more iodine was liberated from KI after the sparge than before. After about five days, treatment of this feed was abandoned.

SECTION VII

TECHNICAL RESULTS

Data Handling

During the period of February through September, 296 complete sets of plant data were obtained for nine feeds divided into a total of 23 groups according to feed and pH. Each complete set of plant data contains 83 recorded quantities (some null). Aside from a thousand or so other data such as BOD, TOC, and nitrogen analyses, the raw technical results from the plant data sets alone are comprised of more than 21,000 individual data.

The analysis and correlation of such a huge quantity of data is feasible only with the aid of an automatic digital computer. An IBM 1130 computer with 8K core memory and magnetic disk file, located at Airco's Murray Hill laboratories, was used.

As described earlier, and in Appendix 6, each complete set of plant data was entered onto a special data sheet by the plant operators. At the end of each week, the data sheets were sent to Murray Hill where the data were punched onto cards. Each data set was then processed by the computer program to yield three or four pages of reduced data for each data set. These weekly analyses of data served to guide further operations of the pilot plant. Also, they were the basis of a preliminary report of this work published elsewhere.(10)

Upon completion of the plant operations in September 1971, all the data sheets and punched cards were carefully checked for accuracy. The results of all COD, ozone concentration, pH, and turbidity analyses had also been recorded in laboratory notebooks which served as a check for the data sheets. And all plant operating parameters could be checked against the independent record in the plant operating log.

Occasionally, some data would be missing from a data sheet. For example, the facilities for COD analyses were limited to two batches of 10 samples per day, including blanks. For this reason, on two of the three data sets normally collected each day, COD analyses were not made on samples from all six reactors. However, the data sheets were encoded to indicate which reactors were not sampled, and the computer program interpolated values for these missing COD's using a procedure described in the next section.

If ozone concentrations in the vent gas or outlet water from any reactor were not measured due to mistake or malfunction, values were estimated from similar and contemporaneous runs. That such values were estimated and not measured was encoded into the data set so that lower statistical weight could be assigned during correlation.

After being carefully checked and the necessary special encoding performed, the complete group of data sets were stored on a magnetic disk file for easy and rapid access by the computer.

All data reduction and correlation programs (about twenty were used) were written in Fortran compiler language. The results of each program were verified by at least one manual computation or by comparison with results of previously verified programs.

COD Reduction Characteristics

Typical COD reduction curves for two plant feeds are shown in Figure 9 in which log COD is plotted vs reaction time

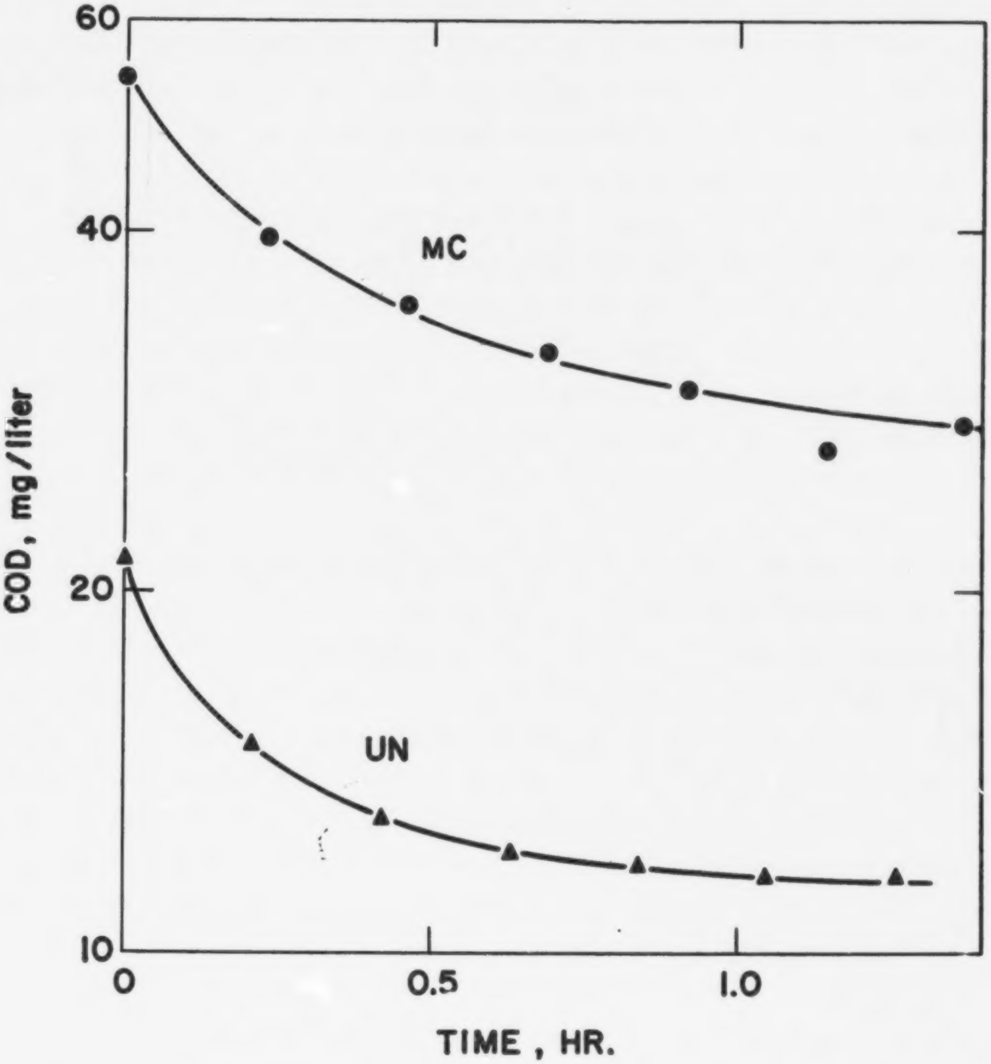

Figure 9. TYPICAL COD REDUCTION CURVES FOR MC AND UN PRETREATED FEEDS: LOG COD vs REACTION TIME

with ozone. Two characteristics are evident. The initial reaction is quite rapid, but as the reaction continues, it slows down so drastically that one might suspect that it has neared completion.

That such is not the case is illustrated in Figure 10 in which log COD (normalized to feed COD) is plotted against log reaction time. These data are for the UN pretreated feed and include end-points from the post-ozonation apparatus, described above. Data for the other feeds yield similar curves. The convex shape of these curves indicates that practically all of the COD can eventually be oxidized by ozone. Thus, in the technical sense, there appears to be no fraction of the COD that is refractory to ozone treatment. However, the reaction becomes so very slow after 50%-70% COD reduction that the economic practicality of further reduction becomes questionable.

There is another interesting, purely empirical way of plotting the pilot plant COD data that is useful because it linearizes the data. In Figure 11 is shown a plot of COD at the outlet of each reactor against the log of the reactor number plus 1.0. These typical data are arbitrarily selected runs on several feeds which cover a wide COD range. The general linear relation is particularly useful for interpolating COD values for reactors which were not sampled for COD in collecting a plant data set. Such a procedure has been used in the data reduction programs.

It must be pointed out, however, that the linearizing scheme in Figure 11 does not, in general, apply when the feed COD points are included in the plot. Thus, the COD from reactor 1 cannot be accurately interpolated from the feed COD and that from reactor 2.

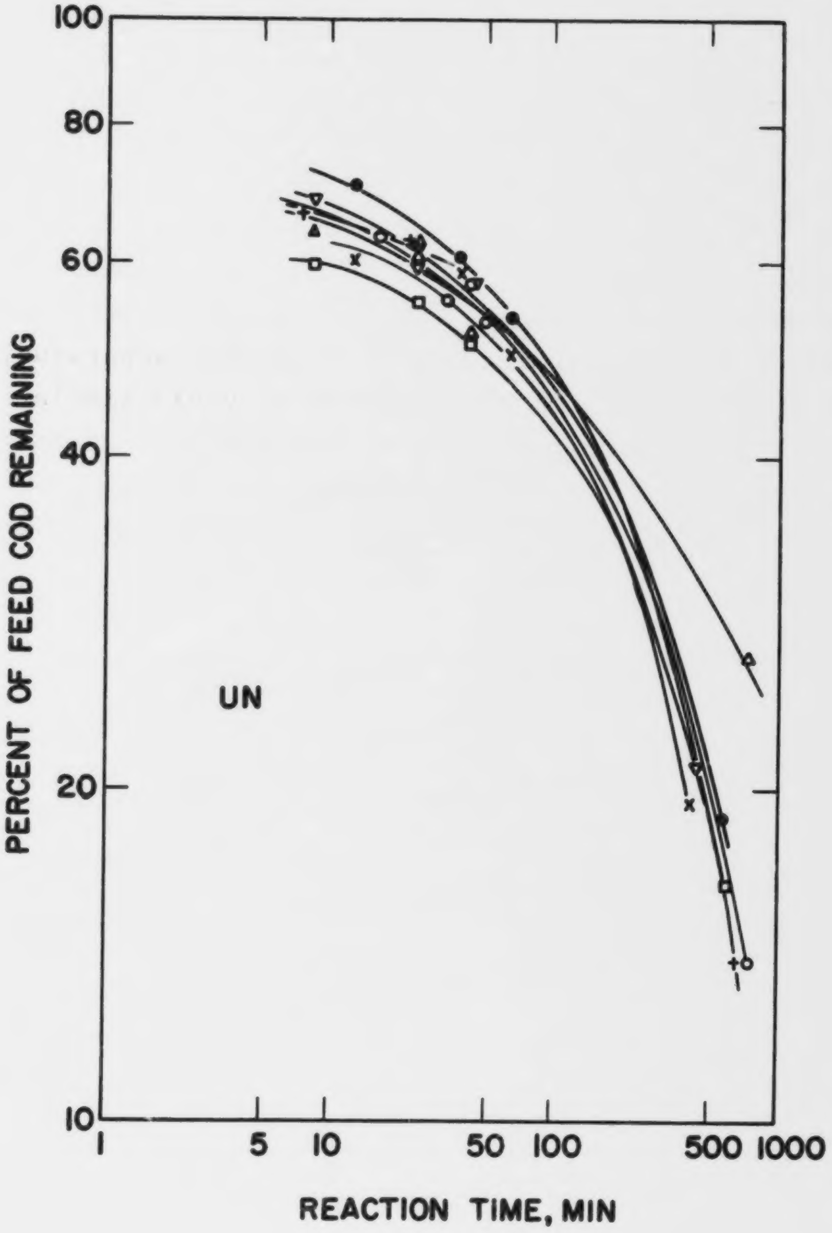

Figure 10. EXTENDED COD REDUCTION CURVES FOR UN PRETREATED FEEDS INCLUDING END-POINTS FROM POST-OZONATION APPARATUS

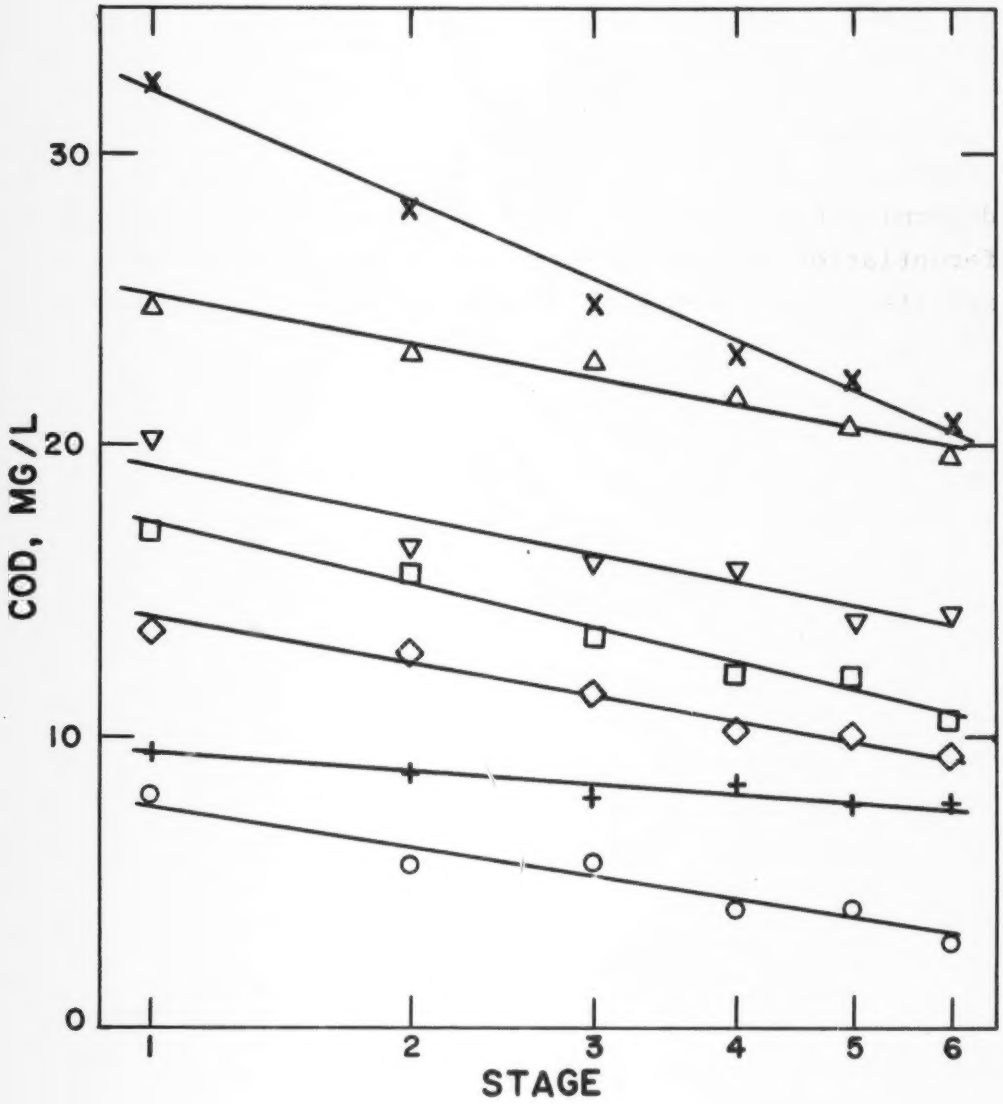

Figure 11. COD REDUCTION vs LOG OF REACTOR NUMBER PLUS ONE

The typical data shown in Figure 11 also qualitatively illustrate the precision and internal consistency of the entire procedure of collecting, handling, and analyzing COD samples. On this sort of linear plot, the raw COD data generally fall within about one mg/l of the average line.

It is also evident from Figure 11 that even with the comparatively high precision in the raw COD data, any attempt to determine COD reduction rates by graphical or numerical differentiation of the raw data would produce badly scattered results. This fact must be considered in selecting methods of correlation.

In the initial computer reduction of each data set, rate data were desired. On the basis of plots similar to Figure 11, the raw COD data were analytically smoothed by a least-square fit to Eq (1) in which a_2 may be zero.

$$L_{N+1} = a_o + a_1 \mathrm{Ln}(N+1) + a_2/\mathrm{Ln}(N+1) \tag{1}$$

where L = COD, mg/l

N = stage number

The nonlinear term is included to permit proper fit to the feed COD [L_1 in Eq (1)].

pH Changes

The pH of the wastewater is an obvious process parameter, and part of the experimental program was devoted to examining its effects.

It was discovered, however, that the pH consistently changes toward neutrality during ozone treatment. In Figures 12, 13, 14, and 15 are shown the pH changes from feedwater to product during many runs on several different plant feeds. In these figures, the circular symbols representing the feedwater pH

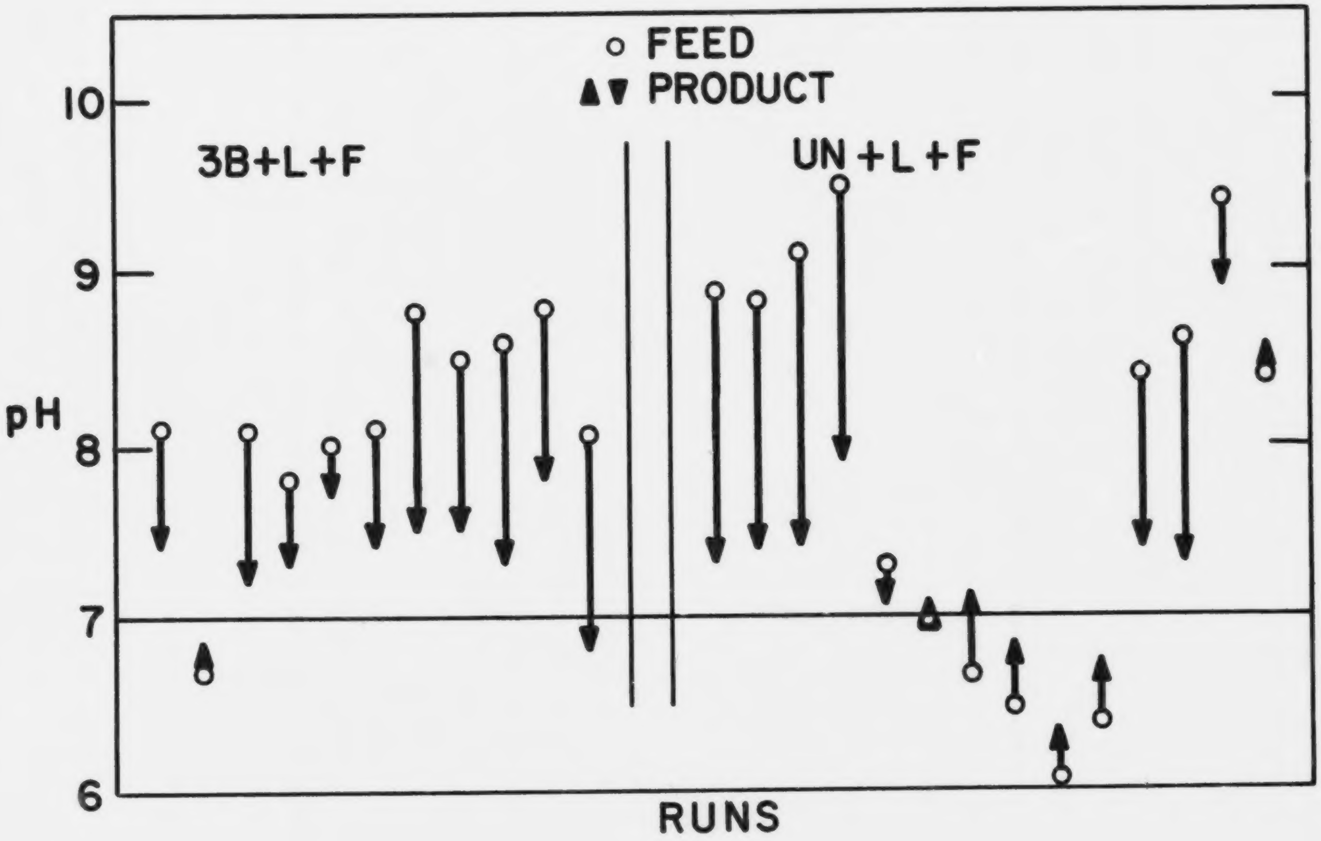

Figure 12. CHANGES OF pH DURING OZONE TREATMENT OF 3B + L + F AND UN + L + F PRETREATED FEED

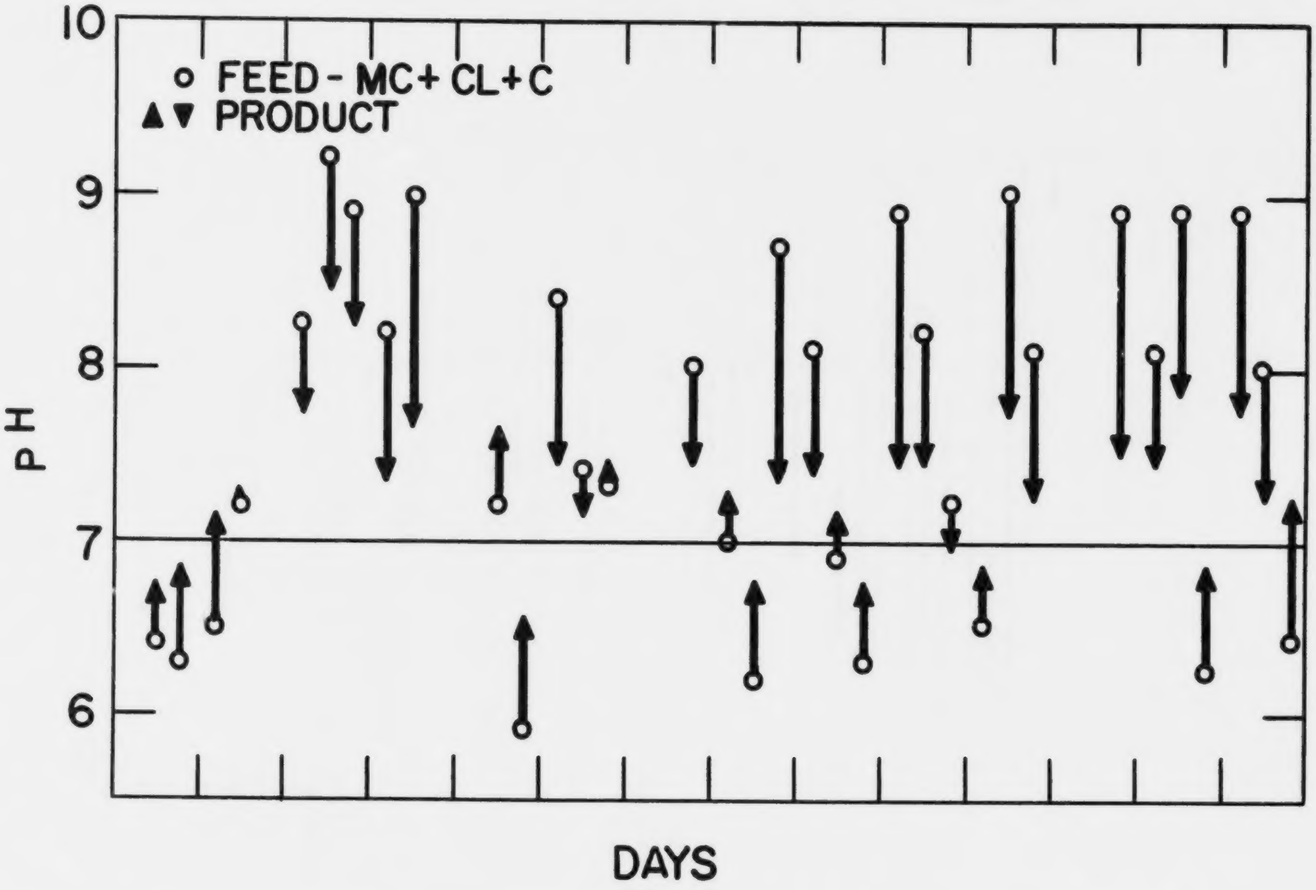

Figure 13. CHANGE OF pH DURING OZONE TREATMENT OF MC + CL + C PRETREATED FEED

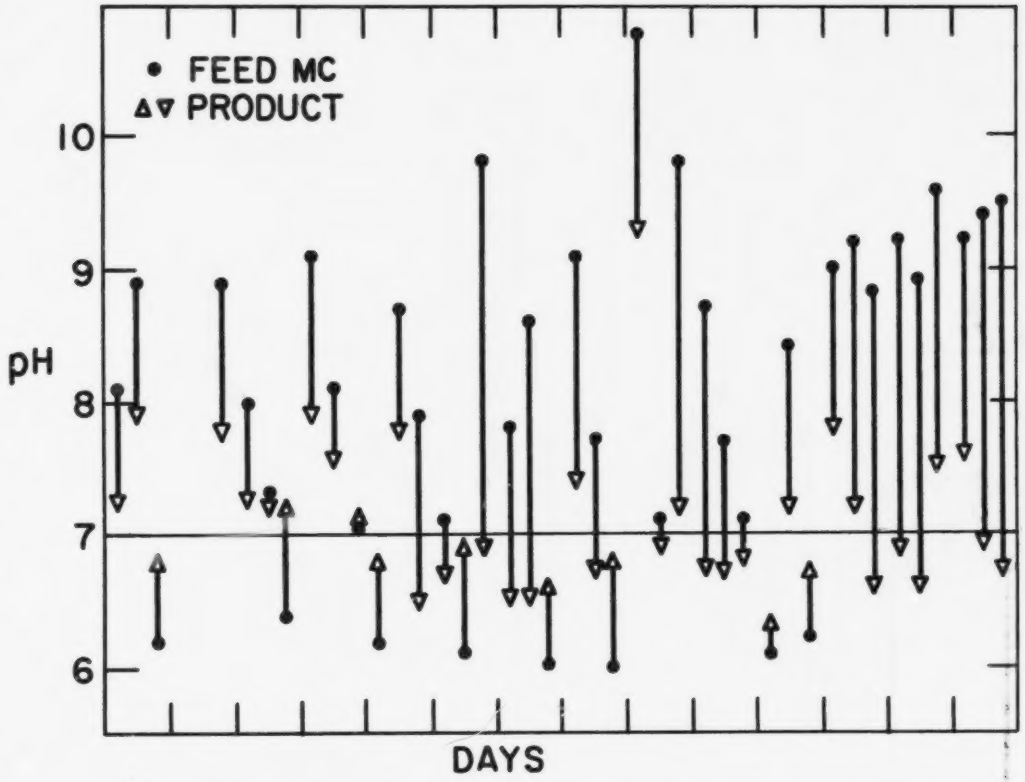

Figure 14. CHANGE OF pH DURING OZONE TREATMENT OF MC PRETREATED FEED

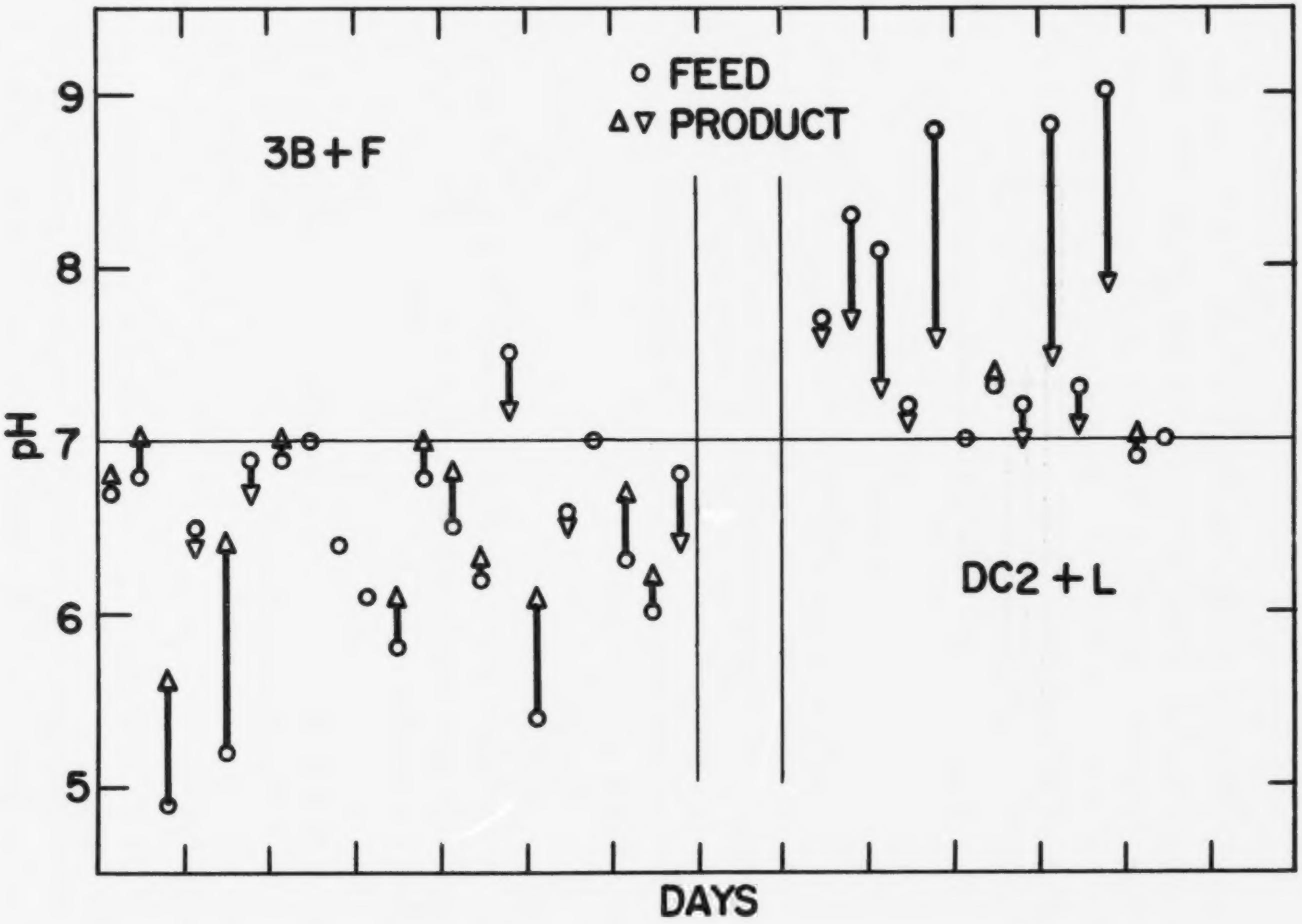

Figure 15. CHANGE OF pH DURING OZONE TREATMENT OF 3B + F AND DC2 + L PRETREATED FEED

are connected by vertical lines to the triangular symbols representing the product water pH. Whether the feedwater is acidic or basic, it can be seen that the product water is almost always nearer neutrality.

While no firm theoretical explanation for the shift of pH toward neutrality has been demonstrated, the phenomenon was consistently observed in the ozone pilot plant, and it has also been noted by others.(11) Limited tests showed that most of the pH change takes place in the initial stages of ozone treatment. And qualitatively, the greater pH changes seem to be associated with the higher COD feeds.

The ozone pilot plant had no provisions for controlling pH throughout the reaction. Therefore, in examining the effects of pH on ozone treatment of wastewater, only the feedwater pH could be used as an independent variable. Throughout this report, pH of a water treated in ozone pilot plant will mean the pH of the water as it entered the first reactor unless explicitly stated otherwise.

Observed COD Reductions

The feed and product COD's observed in all of the complete plant data sets are tabulated in Appendix 6. Feedwater flow rates and pH are also included.

COD data from the post-ozonation apparatus are summarized in Table 4. The total treatment time entries include the ozone treatment time both in the pilot plant and in the post-ozonation apparatus.

Raw Plant Data. It is impractical to show graphs of all the raw COD data and the pH of each set. In order to summarize the data, the data sets for each feed were grouped according

Table 4.

AVERAGE COD RESULTS FROM POST-OZONATION APPARATUS

Feed	No. Runs	Avg COD mg/l	Avg* % Reduction	Avg Total Treatment Time, hr	Avg End pH
UN	12	4.8	82.4	9.17	6.3
MC+CL	4	8.3	83.0	8.43	6.4
3B+F	7	2.6	80.8	8.50	6.5
DC2	10	12.7	88.8	7.65	7.0
DC2+L	3	13.3	83.3	6.93	7.2

---

*Antilog of average of log percent reduction

to pH. These groups were initially selected as integral pH values plus or minus 0.5 pH. The pH values for all data sets within the group were then arithmetically averaged to obtain the average pH for the group.

For each pH group, the COD's corresponding to several selected even values of ozone treatment time were interpolated from the raw COD vs time data using the linearizing scheme described in the discussion of Figure 11. For each of the even times, the interpolated COD's were normalized to feed COD, and all of the resulting values were averaged.

The averages of the COD data interpolated to a common time basis are shown by pH groups and feed pretreatment in Figure 16 through Figure 20. The averaged data fall smoothly, and they all have the same general shape as do the typical individual data sets in Figure 9. In general, the higher pH feeds exhibit more rapid COD reductions. However, one must be careful in drawing quantitative conclusions from these data.

The average representations of the raw data in Figure 16

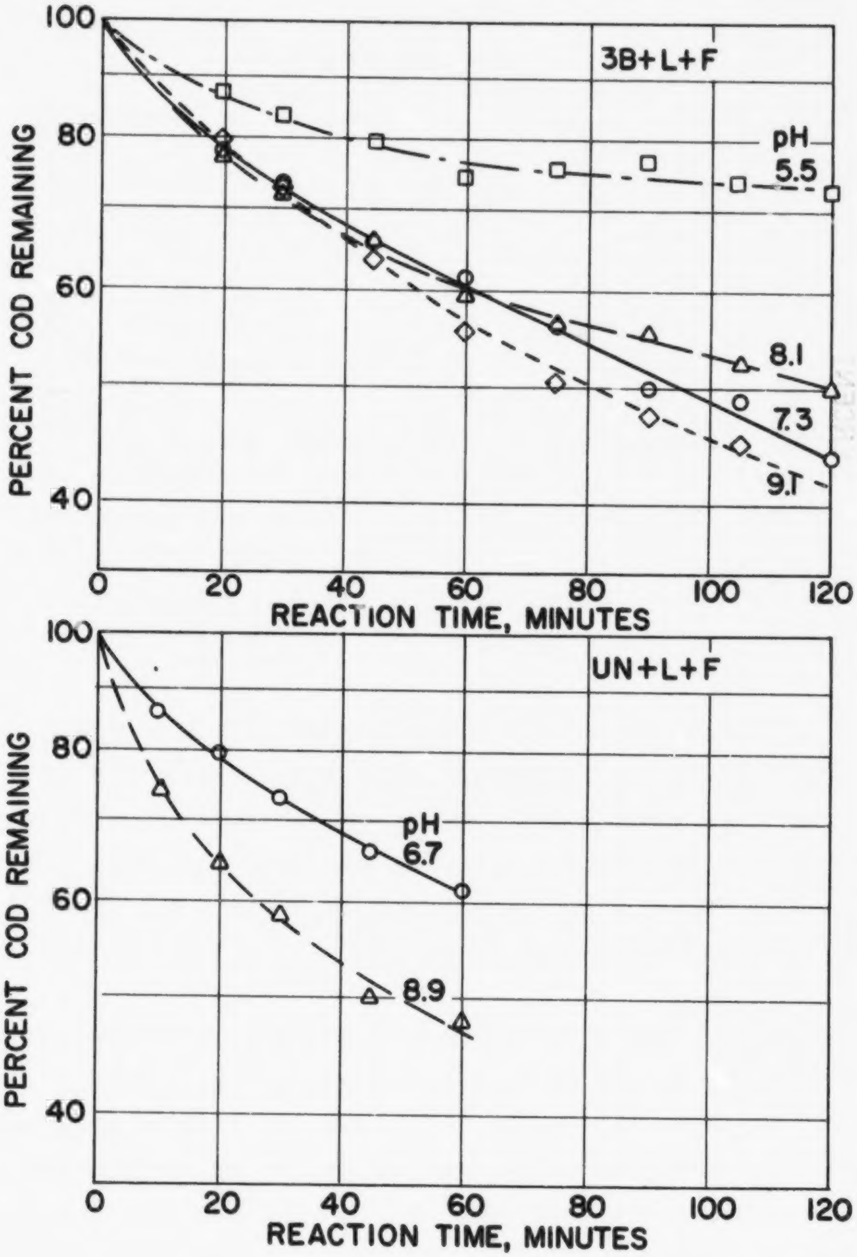

Figure 16. AVERAGE OF PILOT PLANT COD REDUCTION CURVES: 3B + L + F AND UN + L + F

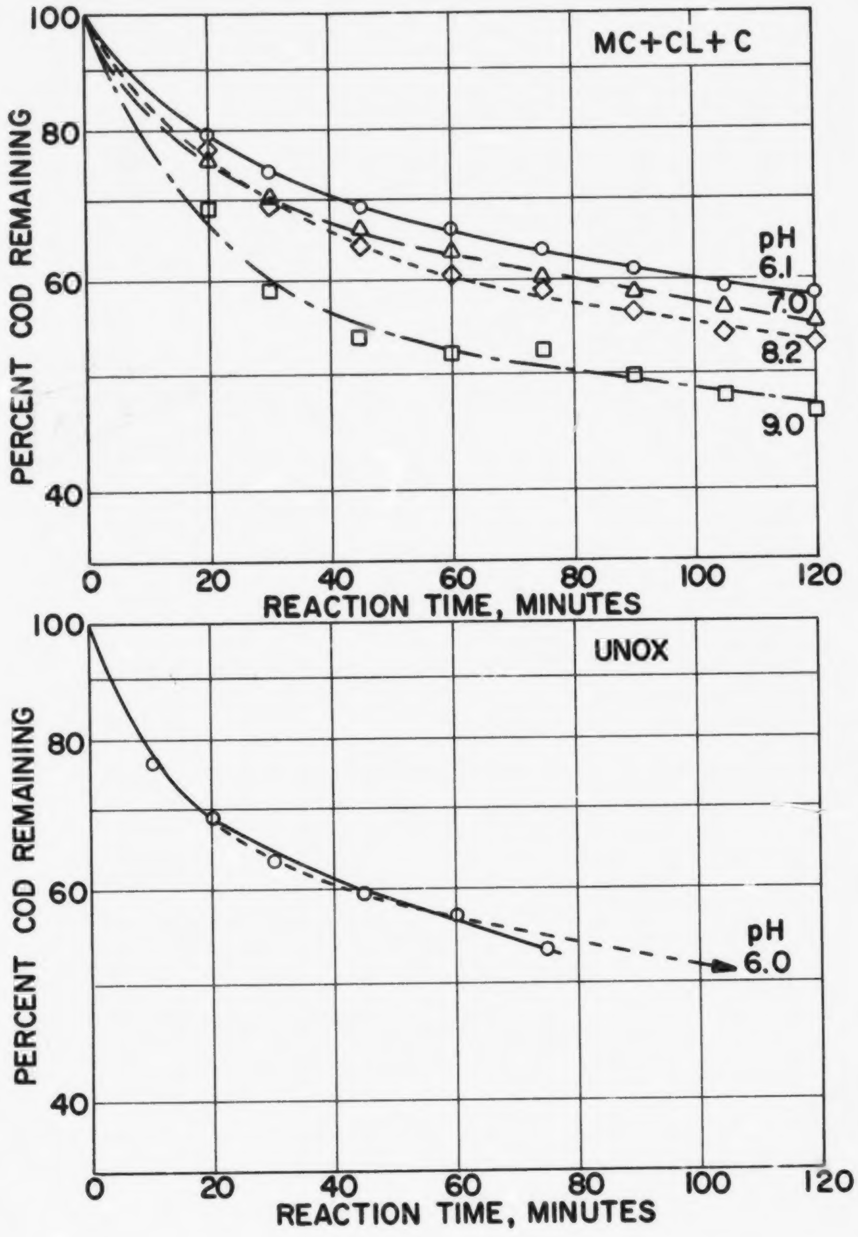

Figure 17: AVERAGE OF PILOT PLANT COD REDUCTION CURVES: MC + CL + C AND UN

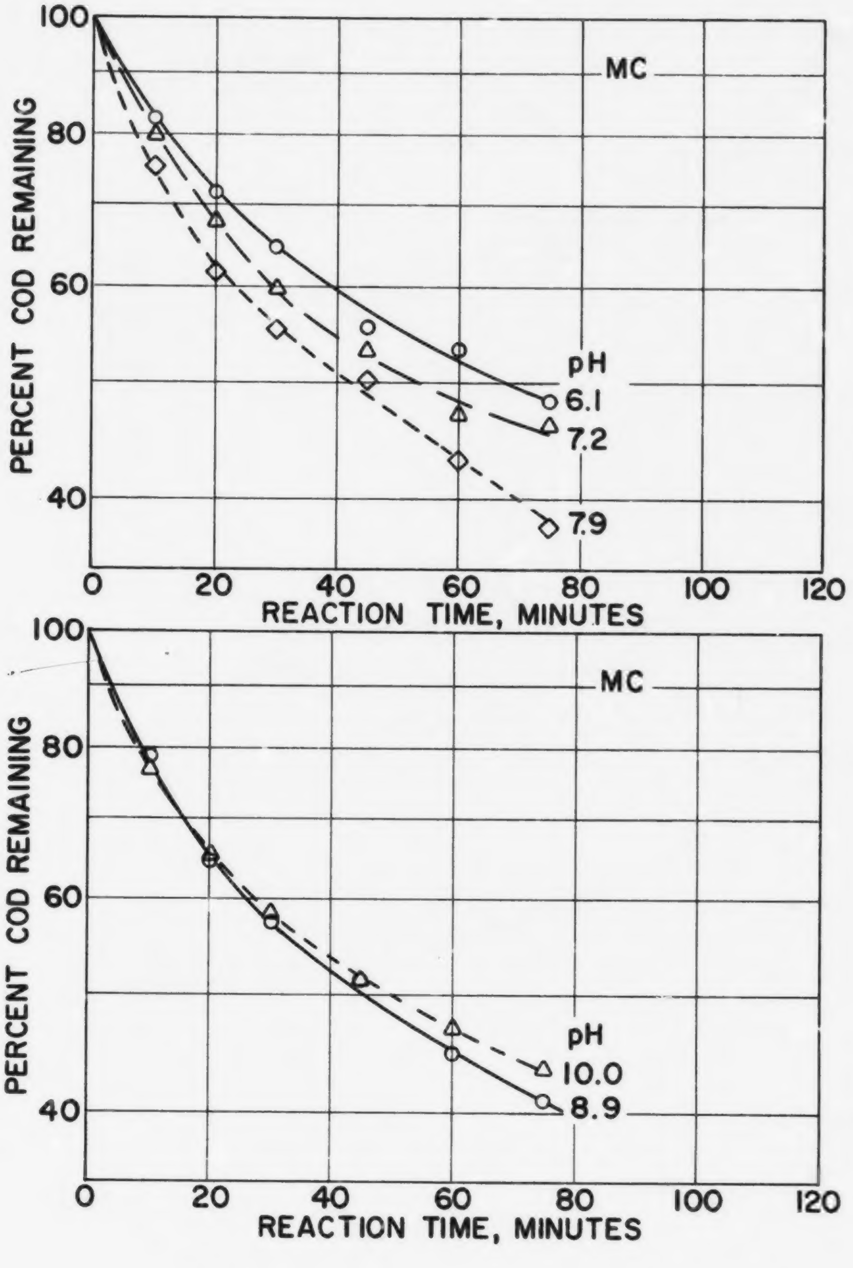

Figure 18. AVERAGE OF PILOT PLANT COD REDUCTION CURVES: MC

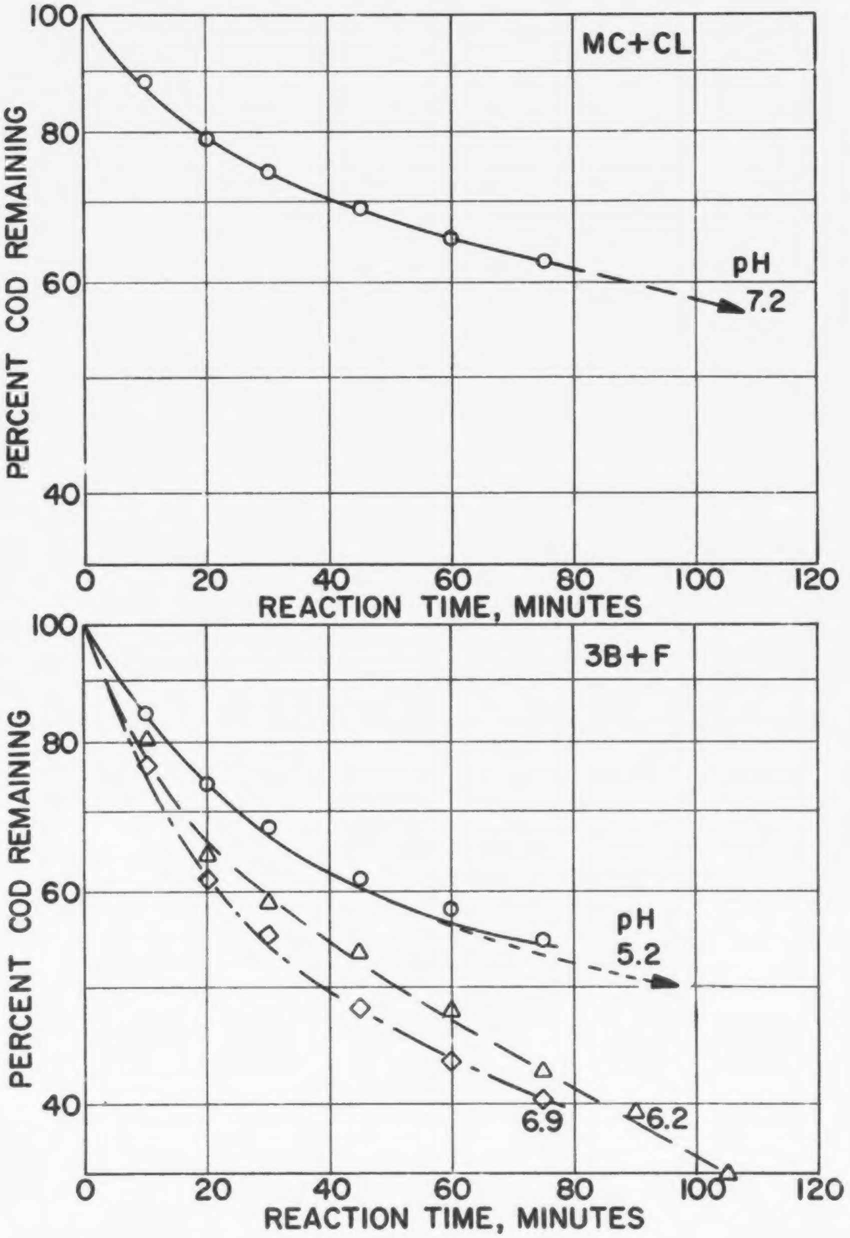

Figure 19. AVERAGE OF PILOT PLANT COD REDUCTION CURVES: MC + CL AND 3B + F

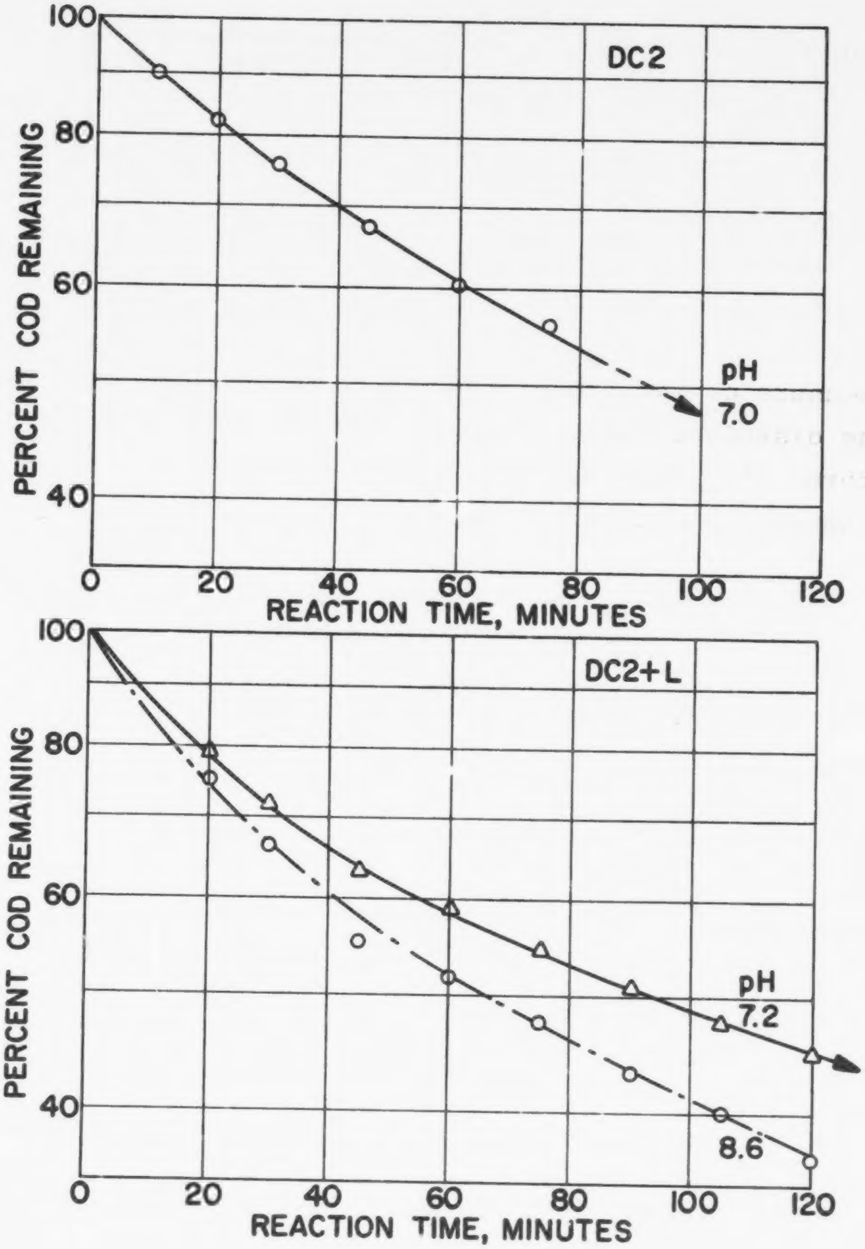

Figure 20. AVERAGE OF PILOT PLANT COD REDUCTION CURVES: DC2 and DC2 + L

through Figure 20 must be taken as nothing more than that. The effect of another very important variable is reflected in these averages, namely, the ozone dosage. Ozone dosage varied from run to run, and from feed to feed. Such variation does not affect the general shape of the curves as is illustrated by the smoothness of the average data. But it does affect the slope of the curves.

One measure of the ozone dosage is the time weighted average of the dissolved ozone concentration at the outlet of the reactors, Z*. This variable will be used in the final correlations and is defined by Eq (2).

$$Z_N{}^* = (\sum_1^N Z_i t_i)/(\sum_1^N t_i) \qquad (2)$$

where $Z_N{}^*$ is evaluated for the outlet of the N-th stage

Z_i is the measured dissolved ozone concentration at the outlet of the i-th stage

t_i is the treatment time in the i-th stage.

For the case of equivolume reactors as in the pilot plant, Eq (2) reduces to Eq (3).

$$Z_N{}^* = (\sum_1^N Z_i)/N \qquad (3)$$

Values of Z* linearly interpolated to a common time base are listed by pH group and feed in Table 5. Even with purely manual control in the pilot plant, it can be seen that the Z* values were held reasonably constant for each pH group. However the values of Z* vary significantly between pH groups and feeds. It is this group to group variation in Z* that is reflected in the averaged raw COD data.

Table 5.

AVERAGE CUMULATIVE DISSOLVED OZONE CONCENTRATION (Z*, mg/l) AT THE OUTLET OF REACTORS

Feed	Avg pH	CUMULATIVE TREATMENT TIME, MIN.				
		20	40	60	90	120
3B+L+F	5.5	2.26	3.03	3.37	3.45	3.49
	7.3	1.68	2.19	2.34	2.46	2.26
	8.1	1.41	2.06	2.28	2.45	2.46
	9.1	0.94	0.89	0.99	1.22	1.16
UN+L+F	6.7	2.89	3.01	2.94	-	-
	8.9	2.18	2.71	2.89	-	-
MC+CL+C	6.1	3.85	3.20	2.80	2.73	2.46
	7.0	3.65	3.14	2.98	2.90	2.68
	8.2	-	2.99	2.77	2.58	2.35
	9.0	-	2.34	2.33	2.37	2.34
UN	6.0	1.70	1.63	1.91	-	-
MC	6.1	1.12	1.28	1.45	-	-
	7.2	1.01	1.21	1.43	-	-
	7.9	0.97	1.14	1.44	-	-
	8.9	0.91	1.05	1.30	-	-
	10.0	0.48	0.75	0.99	-	-
MC+CL	7.2	1.61	1.61	1.66	-	-
3B+F	5.2	2.93	3.31	3.38	-	-
	6.2	4.50	4.79	4.92	5.30	-
	6.9	2.59	3.05	3.25	-	-
DC2	7.0	0.47	0.58	0.67	0.85	-
DC2+L	7.2	0.92	1.36	1.75	2.05	2.08
	8.6	0.36	0.80	1.10	1.35	1.52

"Two Component" Model. The plant data furnish COD reduction values for the first one to two hours of ozone treatment. The POA data furnish an additional point for 7-9 hours treatment. In order to compare these data separated by more than a four to one time ratio, some analytic interpolating function is needed.

An inspection of the data in Figures 16 through 20 suggested that they might be fit by a "two-component" model. The contaminants in the wastewater were assumed to consist of only two components, each exhibiting a different first order reaction rate during ozone treatment. Component 1 was assumed to comprise a fraction x_1 of the contaminants and to have a first order reaction rate constant k_1. Similarly, the $(1-x_1)$ fraction of component 2 had a rate constant k_2. For a first order reaction Eq (4) applies.

$$d \, Ln(L/L_f)/dt = -k \tag{4}$$

For the "two-component" model, Eq (4) can be integrated as follows.

$$L/L_f = x_1 e^{-k_1 t} + (1-x_1) e^{-k_2 t} \tag{5}$$

Implicit here is the assumption that the multistage pilot plant can be approximated as a continuous plug flow reactor.

By a somewhat involved iterative least-square procedure, the values of x_1, k_1 and k_2 were adjusted to fit the average raw COD data for each feed and each pH group. The values so obtained are listed in Table 6. The solid curves shown in Figures 16 through 20 are the least-squares fit of the "two-component" model to the data. From the figures and from the standard deviations, s, listed in Table 6, it is seen that this simple model fits the average data (L/L_f) within about a percent. (See Appendix 7 for a discussion of s.)

Table 6.

FIT OF 2-COMPONENT MODEL TO AVERAGES OF RAW DATA

$$y = x_1 e^{-k_1 t} + (1-x_1) e^{-k_2 t}$$

Feed	pH	x_1	k_1	$(1-x_1)$	k_2	s	n
3B+L+F	5.5	.2631	2.010	.7368	.00698	.018	2
"	7.3	.1626	4.764	.8373	.3243	.012	16
"	8.1	.3095	2.760	.6904	.1623	.010	25
"	9.1	.4466	1.452	.5533	.1754	.008	17
UN+L+F	6.7	.1595	4.601	.8404	.3197	.010	6
"	8.9	.3147	6.422	.6852	.3776	.019	10
MC+CL+C	6.1	.2730	3.268	.7269	.1100	.004	27
"	7.0	.2904	4.224	.7095	.1237	.004	27
"	8.2	.3500	2.936	.6499	.09832	.007	8
"	9.0	.4458	3.705	.5541	.07592	.015	9
MC	6.1	.3314	3.449	.6685	.2632	.012	7
"	7.2	.4408	3.231	.5591	.1785	.010	6
"	7.9	.3157	6.454	.6842	.4560	.011	7
"	8.9	.3492	4.594	.6507	.3646	.012	15
"	10.0	.3438	5.054	.6561	.3304	.003	4
UN	6.0	.2862	7.224	.7137	.2290	.007	34
"	(6.0)	(.3408)	(5.447)	(.6591)	(.1448)	(.012)	(12)
MC+CL	7.2	.2539	3.385	.7460	.1403	.003	12
"	(7.2)	(.2213)	(3.846)	(.7786)	(.1800)	(.006)	(4)
3B+F	5.2	.4767	2.354	.5232	.001465	.023	4
"	(5.2)	(.3722)	(2.891)	(.6277)	(.1387)	(.023)	(7)
"	6.2	.2892	5.609	.7107	.4062	.016	8
"	6.9	.4304	4.342	.5695	.2701	.008	17
DC2	7.0	.2272	1.704	.7727	.3032	.009	21
"	(7.0)	(.3415)	1.354	(.6584)	(.2314)	(.007)	(10)
DC2+L	7.2	.2892	2.362	.7107	.2277	.007	8
"	(7.2)	(.3207)	(2.287)	(.6792)	(.2025)	(.006)	(3)
"	8.6	.3617	2.380	.6382	.2680	.013	5

The values shown in parentheses are for least squares fits including POA data. The values of y and sample deviation, s, are expressed in fraction of feed COD. Times, t, are in hours, thus, the units of k_1 and k_2 are per hour. The values of n not parenthesized are the number of plant data sets averaged. Those in parentheses are the numbers of POA data averaged.

The post-ozonation apparatus was available for only the last five of the nine feeds treated in the ozone pilot plant. For these feeds, the "two-component" model parameters were fitted to the average plant COD data combined with the average data from the post-ozonation apparatus (POA) shown in Table 4. The values so obtained are shown as the parenthesized entries in Table 6 and the results are shown as the broken curves in Figures 17, 19 and 20. The curves fitted to plant and POA data passed within 0.1% of the average L/L_f value from POA, and as can be seen in the figures and from the values of s in Table 6, fitting to both plant and POA data certainly does no violence to the plant data.

In view of the excellent fit of the "two-component" model to the average raw COD data over a range of treatment time from 10 minutes to 8 hours, and COD reduction from 10% to 90%, it is very tempting to draw broad theoretical conclusions. However, because of the uncompensated variations of ozone dosage in the raw data, this probably is not warranted. Instead, the "two-component" model should, for the present, be regarded simply as an excellent empirical relation for fitting and, if necessary, extrapolating COD reduction rate data. For example, if the curves fitted to the plant data alone are extrapolated four to eight-fold in time to predict the POA data, the average predicted percent reduction is within 6% of the experimental POA averages.

Correlations for COD Reduction

General. From detailed inspection of the raw data, one expects the following variables to be important in developing overall correlations for COD reduction by ozone treatment: the nature of the pretreatments given to the wastewater, pH, treatment time, ozone dosage, and dissolved ozone concentrations. There are other, but probably less important, variables such as surface tension, suspended solids, and dissolved inorganic salts. Water temperature is probably an important variable, but one over which there was no control in the pilot plant. Although there was a significant variation in feedwater temperature over the entire period of plant operation, the variation during the treatment of any one feed was insignificant. Therefore, the effects of temperature on reaction rate cannot be included in the overall correlation of the plant data.

Dosage Curves. Ozone dosage is probably the most important variable in determining overall COD reduction. Unfortunately, the term dosage is somewhat ambiguous in general usage. It has been used to mean anything from the quantity of ozone leaving the generator to the net quantity of dissolved ozone consumed in removing COD, and it has been expressed in many different units. To avoid any possibly ambiguity and for the lack of a more precise term, in this report a variable D* is defined as the total pounds of ozone dissolved in the wastewater per pound of COD in the feedwater at the start of the ozone treatment. This is also numerically the same as ppm ozone dissolved/ppm COD feed.

From the plant data, the value of D_i, the pounds of ozone dissolved in the i-th reactor per pound COD feed, is calculated from a gas balance around the reactor.

$$D_i = 0.0828\ G_i\ (c_g - c_v)/100\ M_f \qquad (6)$$

where 0.0828 is the density of oxygen, lb/scf

G_i is the gas flow to the i-th stage, SCFH

c_g is the wt % ozone from generator

c_v is the wt % ozone vented from the i-th stage

M_f is the lb/hr COD feed to the plant

The value of D_N* at the outlet of the N-th stage is simply the cumulative sum of D_i for the case of equivolume stages.

$$D_N^* = \sum_1^N D_i \tag{7}$$

In order to examine the effects of D* on COD reduction, values of D* and L/L_f were interpolated to a common set of selected even values of treatment time. Several sets of the resulting data for individual pH and feed groups were plotted in order to discover a correlating function. A typical such plot is shown in Figure 21. Although the data exhibit scatter as most wastewater treatment data do, the following equation is a good fit to the data at any selected reaction time.

$$\text{Ln } (L/L_f) = -bD^* \tag{8}$$

The next step was to make a least-squares fit of Eq (8) to the data interpolated for the several selected values of reaction time for each pH and feed group. An example of the values of b so obtained are illustrated for the 3B+F feed in Figure 22. In general, this group of graphs showed small, but irregular, variations of b with treatment time and a somewhat larger, but still irregular, variation with pH.

In order to find if the variations of b with time and pH were significant, a simple statistical analysis of the data was made.(12) The values of L/L_f, total reaction time (t*), and D* were calculated for the outlet of each reactor. Only measured COD values were considered; interpolated values were not used.

One adjustment was made of some of the raw data for the DC2+L feed only. After changing the plant inlet plumbing to accept this last feed tested, the feedwater sample tap

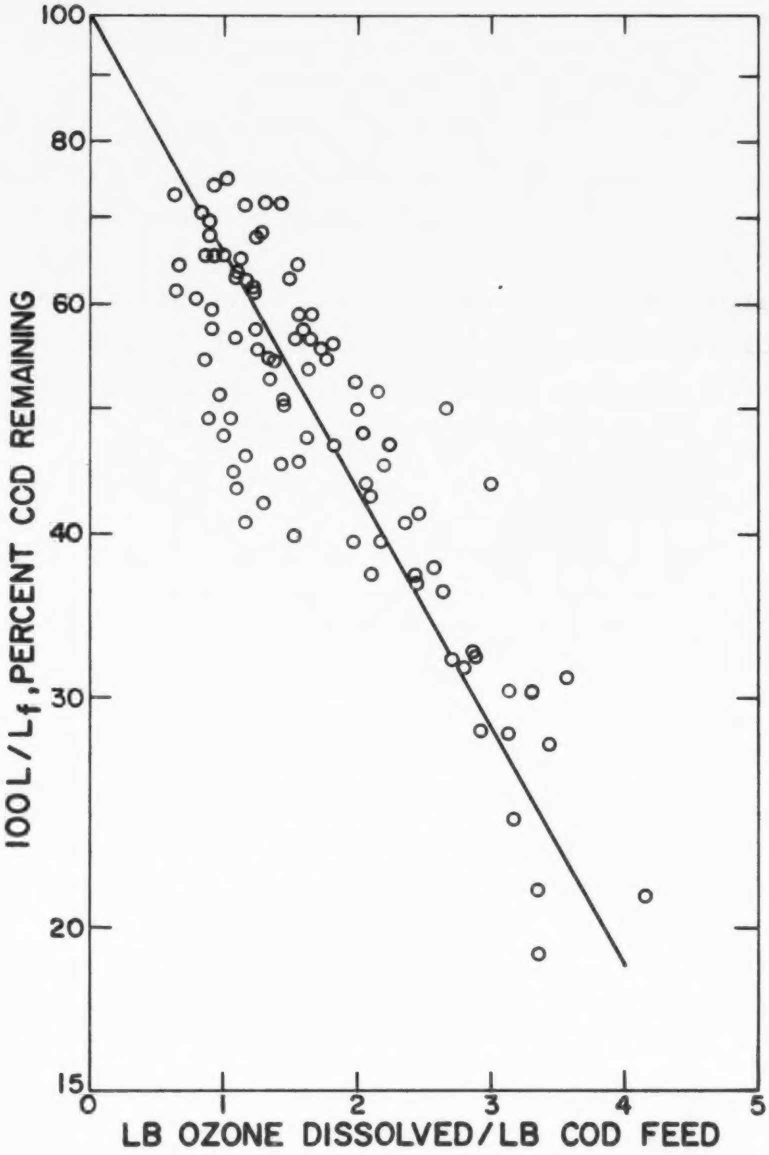

Figure 21. PERCENT COD REMAINING vs OZONE DOSAGE

actually yielded a sample of the water flowing to the first stage mixer, a fact not noticed until the runs were nearly completed. When no recycle was being drawn from the bottom of the first reactor, i.e., when the mixer flow did not exceed the feedwater flow, the tap yielded a good feedwater sample, and no correction was necessary. But when the mixer flow exceeded the feed flow, the tap yielded a mixture of feedwater and recycle water in proportions known from flow meter readings. In this latter case (9 data sets), the feedwater COD was calculated by mass balance from the measured mixture COD assuming that the COD of the recycle water had been reduced by 30% of the measured COD reduction in the entire first stage reactor.

These raw plant data were fit by least squares to the following two equations and to Eq (8) for each pH and feed group separately and then for all points in each feed group.

$$\mathrm{Ln}(L/L_f) = (g + ht)D^* \tag{9}$$

$$\mathrm{Ln}(L/L_f) = (u + j\ \mathrm{Ln}L_f)D^* \tag{10}$$

The resulting parameters for Eq (9) and Eq (8) are listed in Table 7. In this table, s_h represents the standard deviation of the coefficient h in Eq (9), s_b that of coefficient b in Eq (8), and s_e the standard sample deviation. (See Appendix 7.)

The coefficient h in Eq (9) represents the possible variation of b in Eq (8) with reaction time. In general, the standard deviation for h is as large as the value of h. Therefore, it can be concluded that the variation of b with time is insignificant within the 3/4 to 3 hr range of treatment

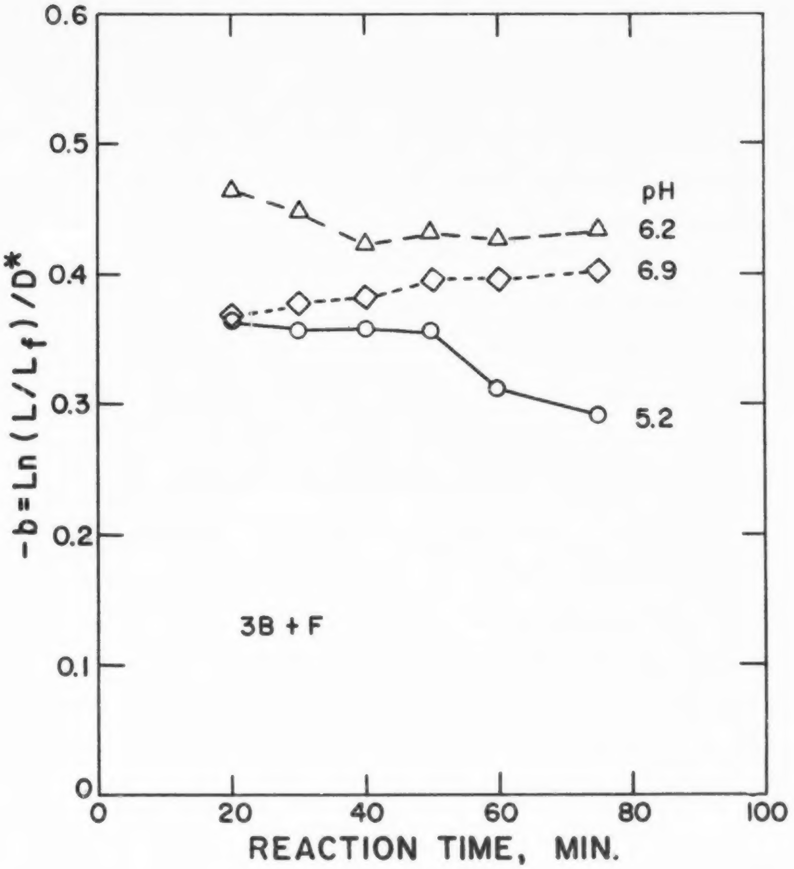

Figure 22. EFFECTS OF pH AND REACTION TIME ON CALCULATED SLOPE (b) OF DOSAGE CURVE: 3B + F

times examined in the pilot plant.

In examining the values of b and s_b in Table 7 it can be seen that, for almost all cases, the difference between b's determined by pH group and the b fitted to all of the pH groups within a feed is less than the combined uncertainty in the b values. Therefore, in the statistical sense, the value of b is not dependent on the pH of the feedwater.

The coefficients for Eq (10) are not shown in Table 7. However, for each feed the values of the coefficients u and j were similar, suggesting that b might depend upon L_f. Therefore, Eq(10) was fitted to the 1031 experimental points for all feeds except 3B+L+F. Those data were not used primarily because at least half the feed COD's contained excess methanol, a substance atypical of domestic wastewater. A good fit was obtained as shown by the coefficient values in Table 7. In figure 23 are shown the b values obtained for each feed plotted against log of the average feed COD. The vertical bars represent the one s_b uncertainty in each value. The point for the 3B+L+F feed is shown by a dotted symbol. And, the solid line represents the fit of Eq(10) to all of the data except 3B+L+F.

The relation between COD reduction during ozone treatment and D* is as follows:

$$\mathrm{Ln}(L/L_f) = (0.1290 - 0.1746\ \mathrm{Ln}\ L_f)\ D^* \qquad (11)$$

Eq (11) is a broad and general relation. According to the analysis of the pilot plant data, the relation between COD reduction and D* is:

a. strongly dependent on the feedwater COD,

b. independent of treatment time within the 0.7 to 3 hour periods examined,

Table 7.

ANALYSIS OF COD REDUCTION vs. D*(LB OZONE DISSOLVED/LB COD FEED)

		$\ln(L/L_f) = (g + ht)D^*$		$\ln(L/Lf) = -bD^*$			
Feed	pH	h	s_h	b	s_b	s_e	No. Points
3B+L+F	5.5	0.101	0.135	-0.168	0.084	0.161	17
	7.3	-0.071	0.161	-0.434	0.074	0.474	89
	8.1	-0.028	0.101	-0.333	0.052	0.472	145
	9.1	0.049	0.038	-0.261	0.022	0.328	95
	All	0.040	0.039	-0.310	0.023	0.443	346
UN+L+F	6.7	0.090	0.080	-0.304	0.047	0.115	30
	8.9	0.115	0.053	-0.315	0.037	0.219	53
	All	0.102	0.047	-0.313	0.028	0.188	83
MC+CL+C	6.1	0.016	0.038	-0.307	0.026	0.173	123
	7.0	0.020	0.044	-0.322	0.029	0.214	116
	8.2	0.012	0.047	-0.307	0.044	0.150	33
	9.0	0.006	0.078	-0.256	0.057	0.351	39
	All	0.014	0.026	-0.295	0.015	0.220	311
MC	6.1	-0.003	0.027	-0.573	0.046	0.089	35
	7.2	-0.053	0.058	-0.580	0.053	0.110	29
	7.9	0.006	0.077	-0.642	0.067	0.141	27
	8.9	-0.076	0.048	-0.570	0.055	0.226	71
	10.0	0.009	0.028	-0.586	0.056	0.080	19
	All	-0.041	0.021	-0.582	0.028	0.166	181
UN (All)	6.0	0.175	0.049	-0.433	0.052	0.263	140
MC+CL(All)	7.2	-0.139	0.061	-0.468	0.080	0.205	49
3B+F	5.2	0.083	0.098	-0.305	0.045	0.190	19
	6.2	-0.054	0.125	-0.471	0.071	0.275	30
	6.9	-0.030	0.090	-0.419	0.043	0.341	75
	All	-0.010	0.064	-0.417	0.032	0.317	124
DC2 (All)	7.0	0.143	0.102	-0.634	0.058	0.206	94
DC2+L (9 data sets adjusted)	7.2	-0.011	0.060	-0.505	0.049	0.124	27
	8.6	-0.075	0.122	-0.650	0.099	0.233	22
	All	-0.038	0.070	-0.568	0.058	0.198	49

All Feeds $\ln(L/L_f) = (u + j \ln L_f)D^*$

$u = 0.1290 \pm 0.0956$

$j = 0.1746 \pm 0.0327$

$s_e = 0.231$

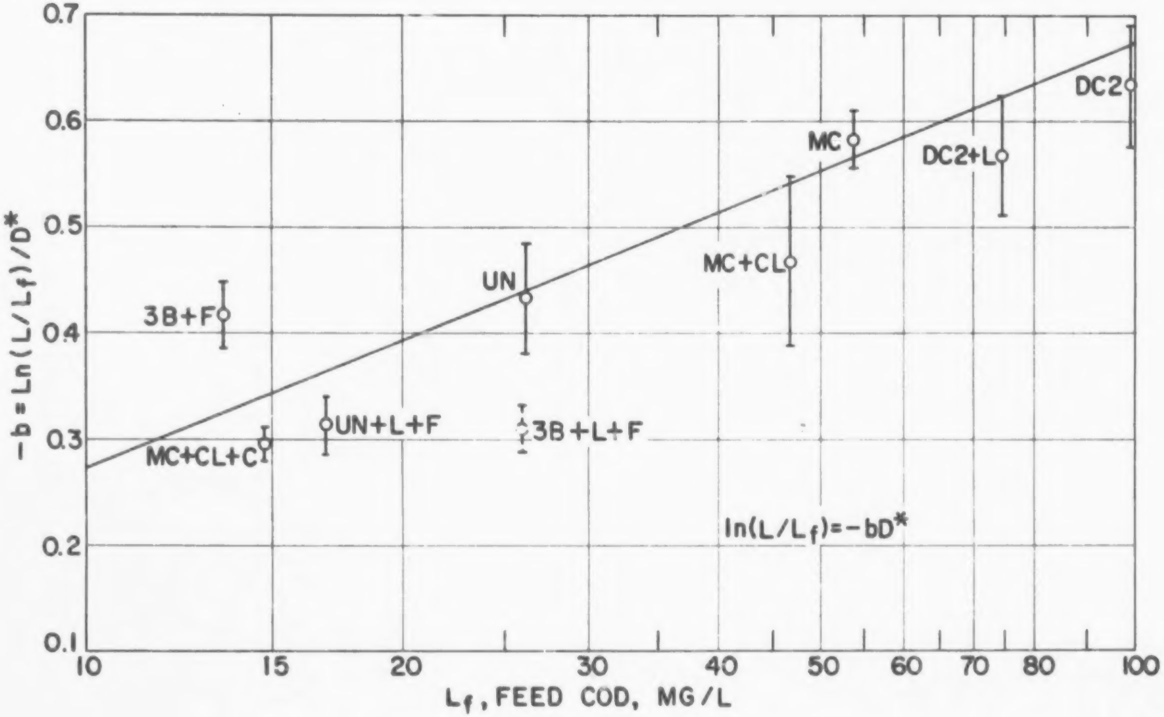

Figure 23. CORRELATION OF COD REMOVAL AND OZONE DOSAGE FOR ALL FEEDS

c. practically independent of the feedwater pH in the range 5 to 10, and

d. practically independent of the exact nature of pretreatment.

To the extent that the Blue Plains wastewater is a typical domestic wastewater, there is no evident reason to expect that Eq (11) should not apply to other wastewaters from mostly domestic sources.

To illustrate some of the implications of Eq (11), the percent COD reduction and the lb ozone dissolved/lb COD removed are shown in Figure 24 as a function of D* for feed COD's of 20, 40, and 80 mg/l. This illustrates that the higher COD feeds are the more susceptible to ozone treatment; a given D* producing a greater percent COD reduction for the higher COD feeds. Similarly, the ozone consumption per unit COD removed is less for the higher COD feeds. This should be expected, especially for oxidative pretreatment, since lower COD feeds reflect more extensive pretreatment and the removal of the more easily oxidizable contaminants.

It must be remembered, though, that D* is normalized to feed COD. To emphasize this, in Figure 25 is shown COD reduction in mg/l as a function of the lb ozone dissolved per 1000 gal water treated. As the feed COD increases, the ozone requirement per 1000 gallons must increase very rapidly to maintain the same percent COD reduction, and even more rapidly to maintain a constant COD product.

COD Reduction Rates

General. Inspection of the averaged raw data and the fact that the dependence of COD removal on D* is time independent suggests that the rate of COD removal at any

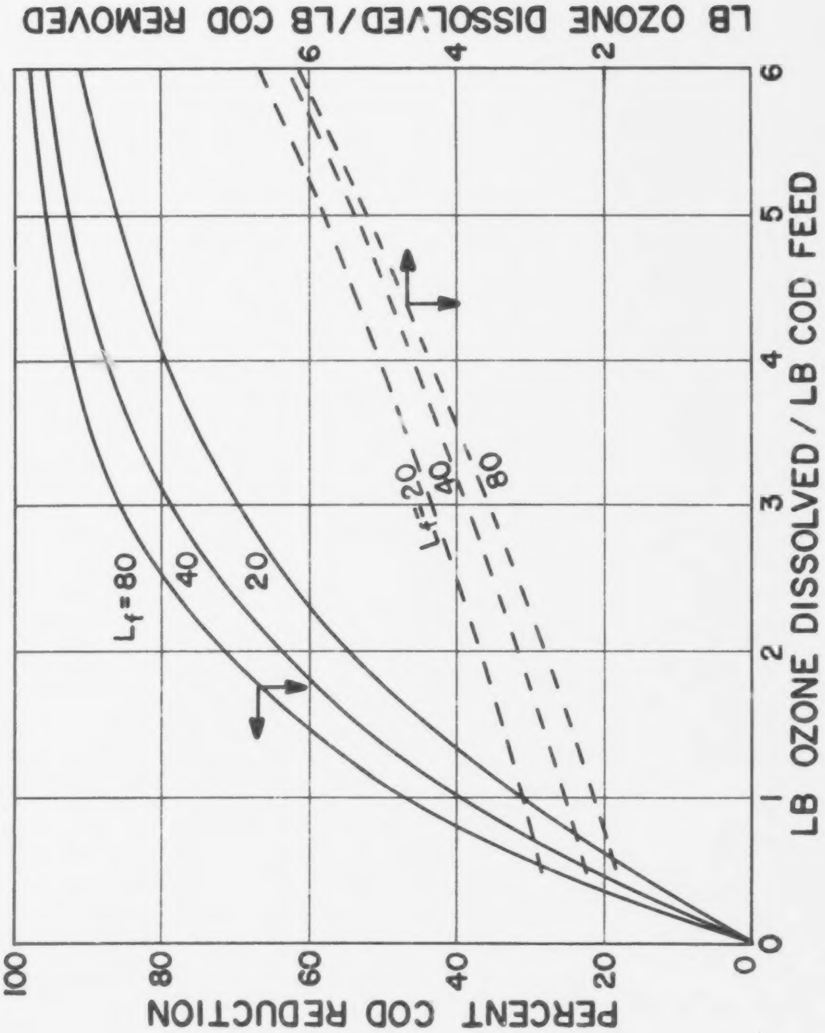

Figure 24. RELATION BETWEEN PERCENT COD REDUCTION AND LB OZONE DISSOLVED/LB COD FEED AND LB OZONE DISSOLVED/LB COD REMOVED

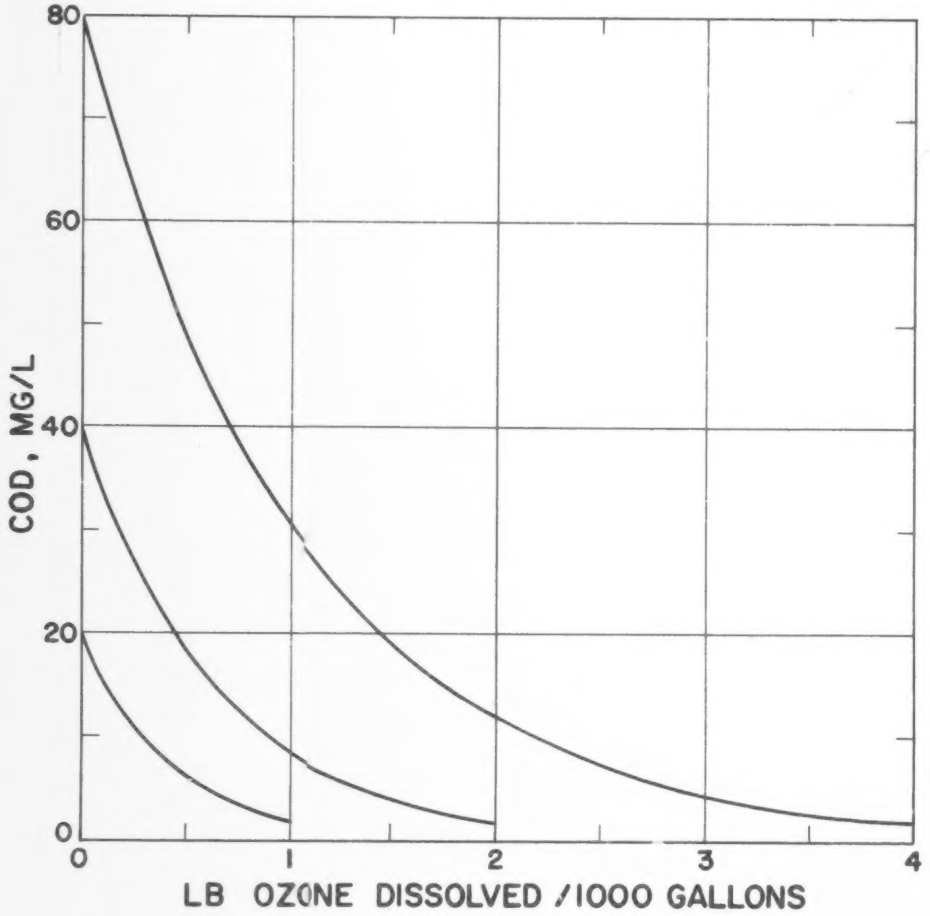

Figure 25. COD IN MG/L vs LB OZONE DISSOLVED PER 1000 GAL WATER TREATED

point during ozone treatment is strongly dependent on the degree of ozone treatment up to that point. Thus, the correlation of COD reduction rates must be made on an integral, rather than a differential, basis.

Seeing that COD reduction as a function of D* exhibits no significant pH dependence, but that the averaged raw data do depend on pH, it is evident that pH must have an important effect on the COD reduction rate.

From simple chemical intuition, the reaction rate should also depend on the dissolved ozone concentration. The dissolved ozone concentration varied throughout each reactor, that at the bottom of the reactor being higher than that at the top, and one should expect that in the mixer and dissolver tube the concentrations were higher still. Presumably, there is some more-or-less constant relationship between dissolved ozone concentrations at various locations within the reactor. Because only dissolved ozone values at the reactor outlets could be obtained for all plant data sets, these values were selected for use in correlating the data. As was pointed out above, dissolved ozone concentrations measured by the acidic KI procedure prior to 6/24/71 are considerably less reliable than those measured by the alkaline KI procedure after that date. For this reason, only the plant data sets collected after 6/24/71 were used for the reaction rate correlation. It should be noted that the latter period includes the complete range of feed COD's from the lowest, 3B+F, to the highest, DC2.

Having recognized, though, that the reaction rate correlation must be on an integral basis in order to take into account the previous history of ozone treatment up to any point, one must use some integral function of the dissolved ozone concentration at the outlet of each reactor. Z* (the time weighted average of dissolved ozone concentration) as defined by Eq (3) is just such a function.

A reaction rate correlation implies the use of COD removal as the dependent variable. But because COD removal is a simple function of D* and L_f, one independent variable, L_f, can be eliminated from the reaction rate correlation by using D* rather than L/L_f as the dependent variable. Moreover, the use of D* has certain advantages in the curve-fitting mathematics. Any correlated value of D* can be simply related to COD reduction using Eq (11).

For the reasons outlined above, the general "reaction rate" correlation will be aimed at describing D* as a function of cumulative reaction time, t*; pH of the entering feedwater; and Z*. (It should be noted that time, t, in all equations is in hours, whereas the time axes are in minutes for all data or correlation plots which follow.)

Average Raw Data. By pH and feed groups, the raw plant data for the period after 6/24/71 were used to obtain interpolated values of Z* and D* at selected even values of treatment time. (The data for the MC+CL feed were not used because the residual chlorine destroyed the accuracy of the dissolved ozone measurements.) These interpolated data were plotted on various coordinates and it was found that on log Z* vs log D* plots the data fell linearly. A typical plot is shown in Figure 26 for all data in the pH range 6.5 to 7.5 interpolated for 60 min treatment time. Although there is some scatter, the data for all five feeds clearly fall along a straight line.

The next step was to least-square a straight line through the interpolated log Z* and log D* data for all points in each pH group and for each common value of reaction time. From these smoothing functions, the values of D* could be interpolated for a number of selected even values of Z*, t*, and pH. In Figure 27 is shown a plot of the smoothed and interpolated values of D* vs t* for Z* = 1 mg/l and for three pH groups. (Recognize that each group contains data for several different feeds.) Plots for other values of Z* yielded curves of similar shape but displaced upward with increases in Z*. Thus, in Figure 27 one can see an approximation of the shape that the "reaction rate" correlation curves must assume. Log D* vs log t* is a straight line for pH 7. Other pH curves initially diverge from the pH 7 curve, but then begin approaching the pH 7 values as treatment time is increased. This characteristic is entirely consistent with the observed change of pH toward neutrality during ozone treatment.

Final Correlation. The final correlation of D* as a function of t*, pH, and Z* was obtained using a more-or-less standard multiple-regression procedure (13) modified to discard "wild points" (2.5 s criterion) from the initial fit before making the final fit. Only raw experimental data were used. In the few cases that either Z* or D* incorporated estimated data, the point was assigned 1/2 normal statistical weight. If both incorporated estimated data, the statistical weight 1/4 was assigned.

$$\text{Ln } D^* = a_o + a_1 \text{ Ln } t^* + a_2 \text{ Ln} Z^* + a_3 (pH-7)/t^* + a_4[(pH-7)/t^*]\text{Ln } t^* \quad (12)$$

where $a_o = 0.0072 \pm 0.0137$

$a_1 = 0.4461 \pm 0.0156$

$a_2 = 0.5044 \pm 0.0147$

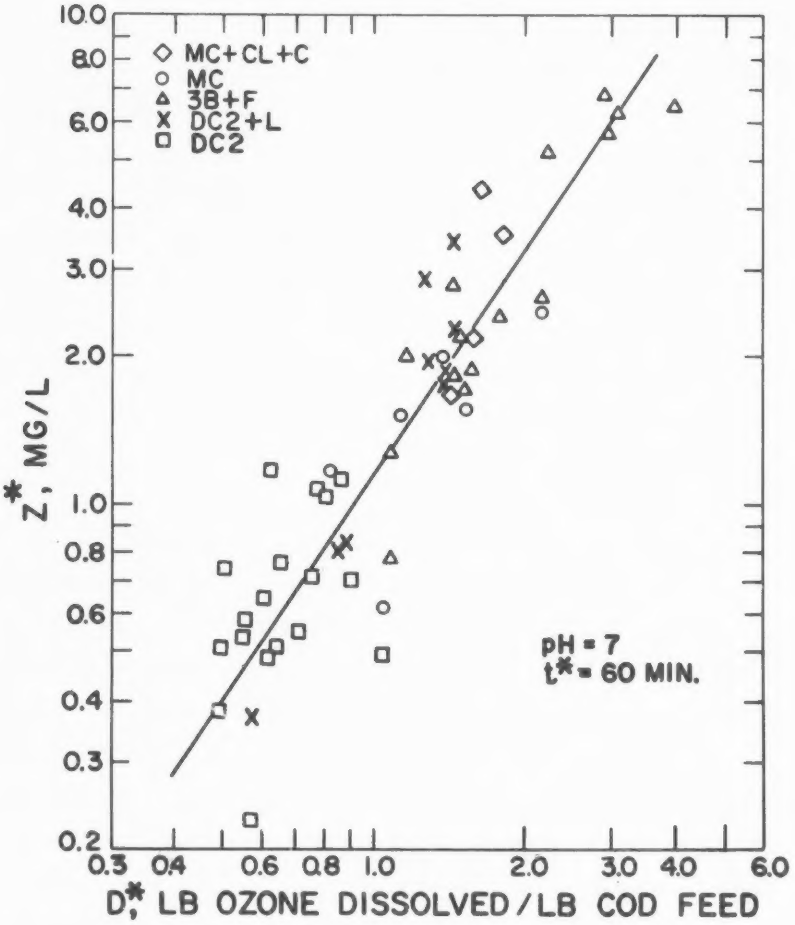

Figure 26. PLOT OF LOG DISSOLVED OZONE (Z*) vs LOG DOSAGE, D*

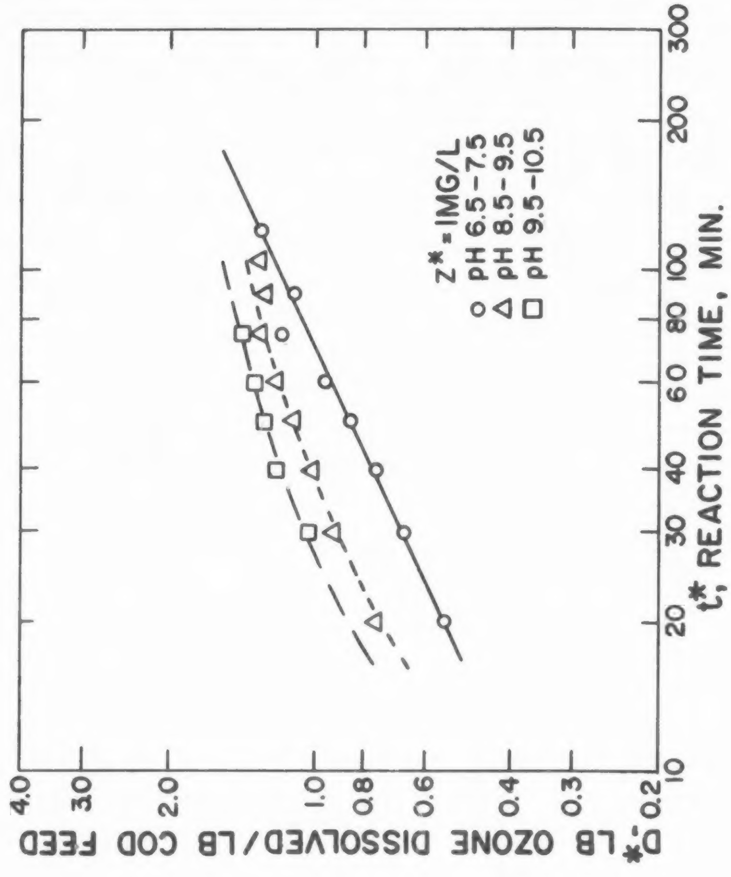

Figure 27. RELATION BETWEEN SMOOTHED VALUES OF DOSAGE (D*) AND REACTION TIME (t*) FOR Z* = 1 MG/L AND INDICATED pH

$$a_3 = 0.1359 \pm 0.0094$$

$$a_4 = 0.0575 \pm 0.0067$$

The coefficients were obtained from a final fit to 774 experimental data points after discarding 23 points as "wild". The standard sample deviation on ln D* is 0.267, thus the D* data scatter about 30% around this function. The uncertainty shown for the coefficients are the one s_a values. Note that for practical purposes, a_o is zero.

In Figure 28, Eq (12) is graphed for the value Z* = 1 mg/l. Figure 29 is a graph of Eq (12) for pH 7. From Eq (12) it may be noted that the displacement of the curves due to pH is independent of Z*, thus by the use of conventional graphical techniques, the values for any set of D*, t*, and Z* can be determined from Figures 28 and 29.

Eq (11) can be combined with Eq (12) to yield an actual reaction rate function.

$$\mathrm{Ln}(L/L_f) = (0.1290 - 0.1746\ \mathrm{Ln}L_f)\,t^{*\,(0.4461 + 0.0575(pH-7)/t^*)}\,Z^{*\,0.5044}\,e^{0.1359\,(pH-7)/t^*} \quad (13)$$

For pH = 7, Eq (13) is simplified to Eq (14)

$$\mathrm{Ln}(L/L_f) = (0.1290 - 0.1746\ \mathrm{Ln}L_f)\,Z^{*\,0.5044}\,t^{0.4461} \quad (14)$$

Again, to the extent that the Blue Plains wastewater is typical of domestic wastewater, there is no evident reason to expect that Eq (14) should not hold for other domestic wastewaters. But because wastewater streams vary in their pH buffering capacity, Eq (13) is probably not so generally applicable for pH values much removed from neutrality.

Applying the Correlations. In order to illustrate the use of the correlated data, a specific example will be used. Consider an ozone treatment plant receiving a pretreated waste from primarily domestic sources with a COD of 40 mg/l and a pH of 7. The required product COD is 20 mg/l. Assume that the plant will consist of three equivolume reactors each with a detention time of 15 minutes.

Total Ozone Dissolved. From Eq (11) or Figure 23, the value of -b for domestic wastewater with $L_f = 40$ is 0.513. From Eq (10) or (11) or Figure 24, the required value of D* for $L/L_f = 0.5$ is 1.35 lb ozone dissolved/lb COD feed (or 54 mg/l). From Eq (12) or Figure 29, attaining D* of 1.35 in 45 min (3x15 min) at pH 7 requires a Z* of about 2.3 mg/l.

Ozone Dissolved per Stage. The only technical requirement for the values of Z_i in each of the three stages is that Eq (3) be satisfied, i.e., $Z_1 + Z_2 + Z_3 = 3 \times Z^*=6.9$ mg/l. Without economic optimization, there are no further requirements.

For this example, the following Z_i values will be used: $Z_1 = 1.4$, $Z_2 = 2.5$, $Z_3 = 3.0$ mg/l. Again using Eq (14) or Figure 29, D_1^* at $t_1^* = 0.25$ hr and $Z_1^* = 1.4$ mg/l is 0.63. D_2^* at $t_2^* = 0.50$ hr and $Z_2^* = (1.4 + 2.5)/2=1.95$ mg/l is 1.02. And D_3^* at $t_3^* = 0.75$ hr and $Z^* = 2.3$ mg/l is, of course, 1.35.

Recognizing from Eq (3) that $D_i = D_i^* - D_{i-1}^*$, the lb ozone dissolved/lb feed COD in each of the three reactors is 0.63, 0.39, and 0.33, respectively.

To proceed, this example will be placed on a 1000 gal treated basis. The COD feed is 40 lb COD/10^6 lb water x 1000 gal x 8.33 lb/gal = 0.333 lb COD feed/1000 gal. The quantity of ozone to be dissolved is 1.35 x 0.33 = 0.45 lb ozone/1000 gal

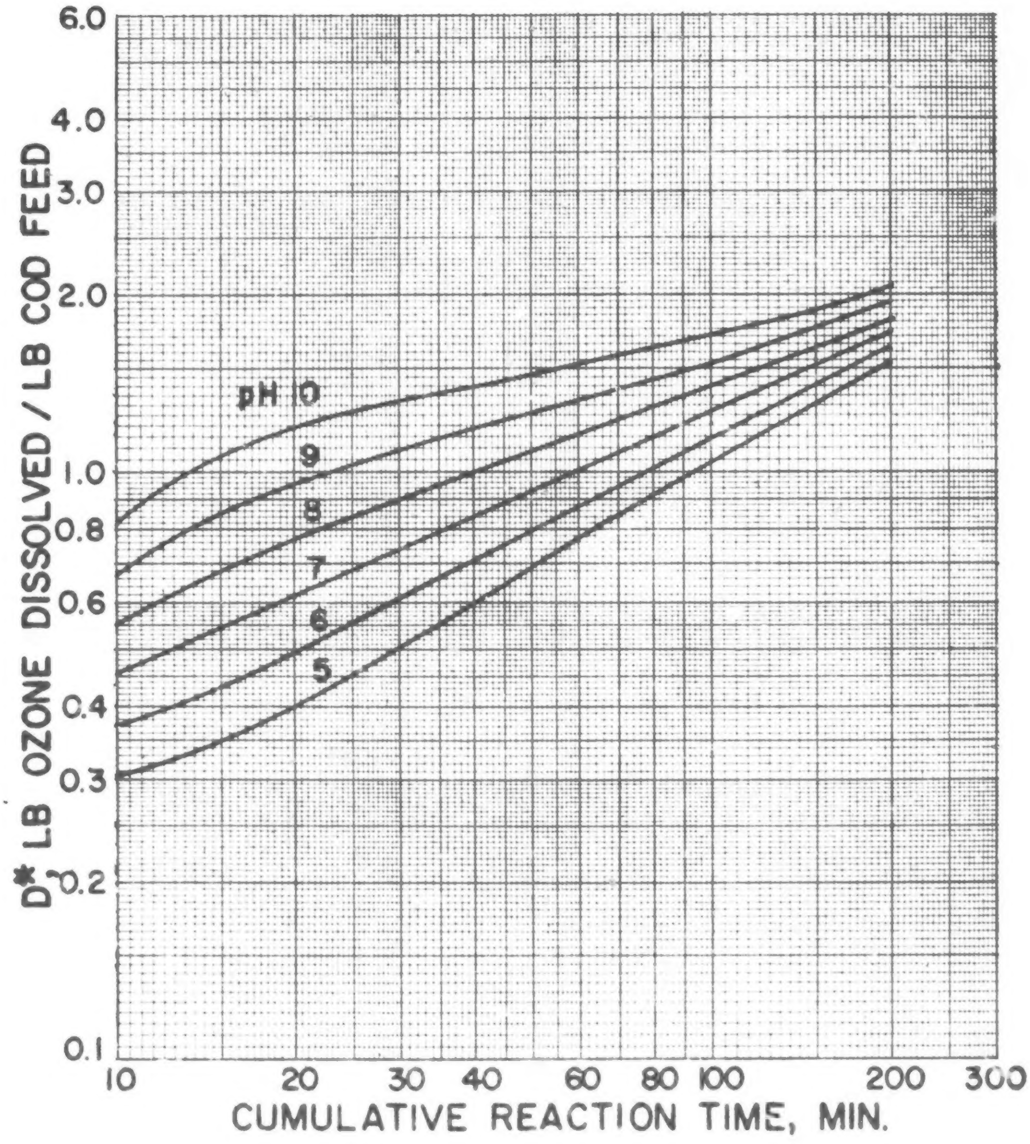

Figure 28. GRAPH OF REACTION RATE CORRELATION FOR CONSTANT Z* = 1 MG/L

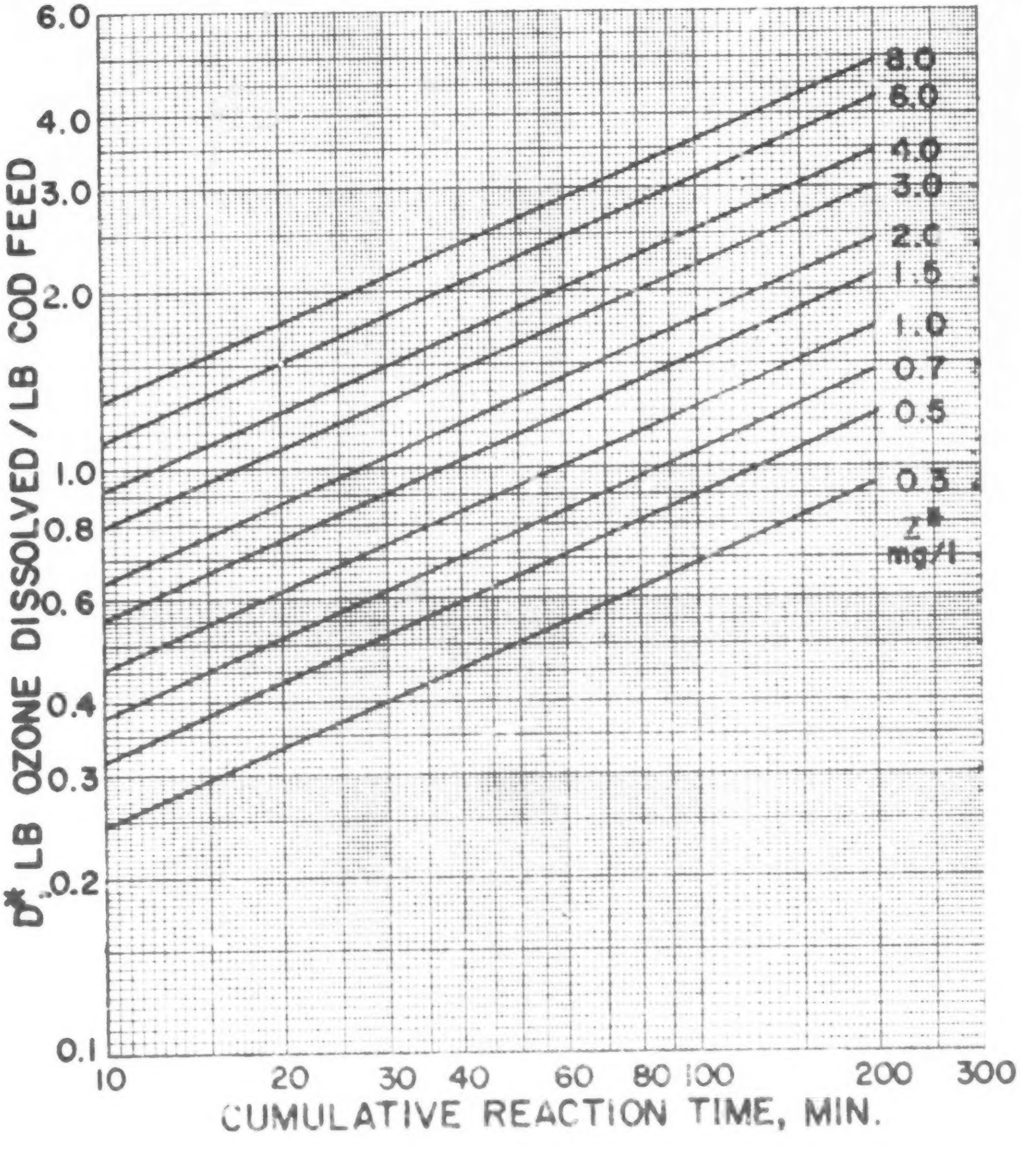

Figure 29. GRAPH OF REACTION RATE CORRELATION FOR CONSTANT pH 7

treated, 0.21 in the first stage, 0.13 in the second stage, and 0.11 in the third stage.

Oxygen Consumption

There are four sources of oxygen consumption in the ozone pilot plant.

1. Chemical reaction of ozone to reduce COD: one lb of oxygen is required to remove one lb COD.
2. Dissolution of oxygen in the product water: after deaeration, the feedwater contains practically no dissolved oxygen, and the product water is practically saturated with one atma of pure oxygen.
3. Dissolution of oxygen and residual ozone gas in the compressor seal water.
4. System leakage, including gas sampling.

Make-up oxygen to the pilot plant was measured by an integrating, positive displacement meter. The meter readings (usually about 25 cu ft/hr) were generally in agreement with the oxygen consumption calculated for items 1, 2, and 3, above, which indicates that system leakage was small. Oxygen losses in the compressor seal water, which accounted for roughly 40% of the total oxygen consumption, could be eleminated either by recycling the seal water to one of the latter treatment stages or by using a different type of compressor.

Nitrogen Reactions

The reactions of nitrogenous substances in wastewater during ozone treatment were investigated to a limited extent for the last five feedwaters tested in the pilot plant: UN, MC, 3B + F, DC2, and DC2 + L. Usually, one set of wastewater samples per day were collected and submitted to the EPA analytical group for nitrogen analyses. The samples were analyzed for total Kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3-N), nitrite nitrogen (NO_2-N), and nitrate nitrogen (NO_3-N).

In general, ozone treatment did not reduce the overall nitrogen content of the wastewater. At high pH values, however, some of the ammonia and total Kjeldahl nitrogen was oxidized to nitrates. No nitrite formation was ever observed. Interestingly, there was no detectable ammonia removal in the vacuum deaerator, even at high pH values.

The nitrogen analytical data for five feedwater pretreatments are summarized in bar chart form in Fig 30 through 33. Each bar in these figures represents the average results for a number of pilot plant runs, and each bar is subdivided into TKN, NH_3-N, and NO_3-N. Bars are shown for the feedwater, water from the outlet of the first reactor (#1), and water from the outlet of the last reactor (#6).

UN. Average results for the Unox pretreated wastewater are summarized in Fig 30. The feedwater was fairly well nitrified by the pretreatment, and ozone treatment at pH 5.9 to 6.6 produced no significant additional nitrification.

MC. Average results for the feedwater pretreated by mineral clarification is shown in Fig 31 for three different pH values. Pretreatment had oxidized very little of the nitrogenous materials. These data illustrate the strong dependence of nitrification by ozone treatment on feedwater pH. Nitrification is significant only at pH 10 and in the final stages of the treatment process. At pH 6, only about 5% of the TKN was oxidized to nitrate by ozone; only about 8% was oxidized at pH 9; but more than 35% of the TKN was nitrified by ozone at pH 10.

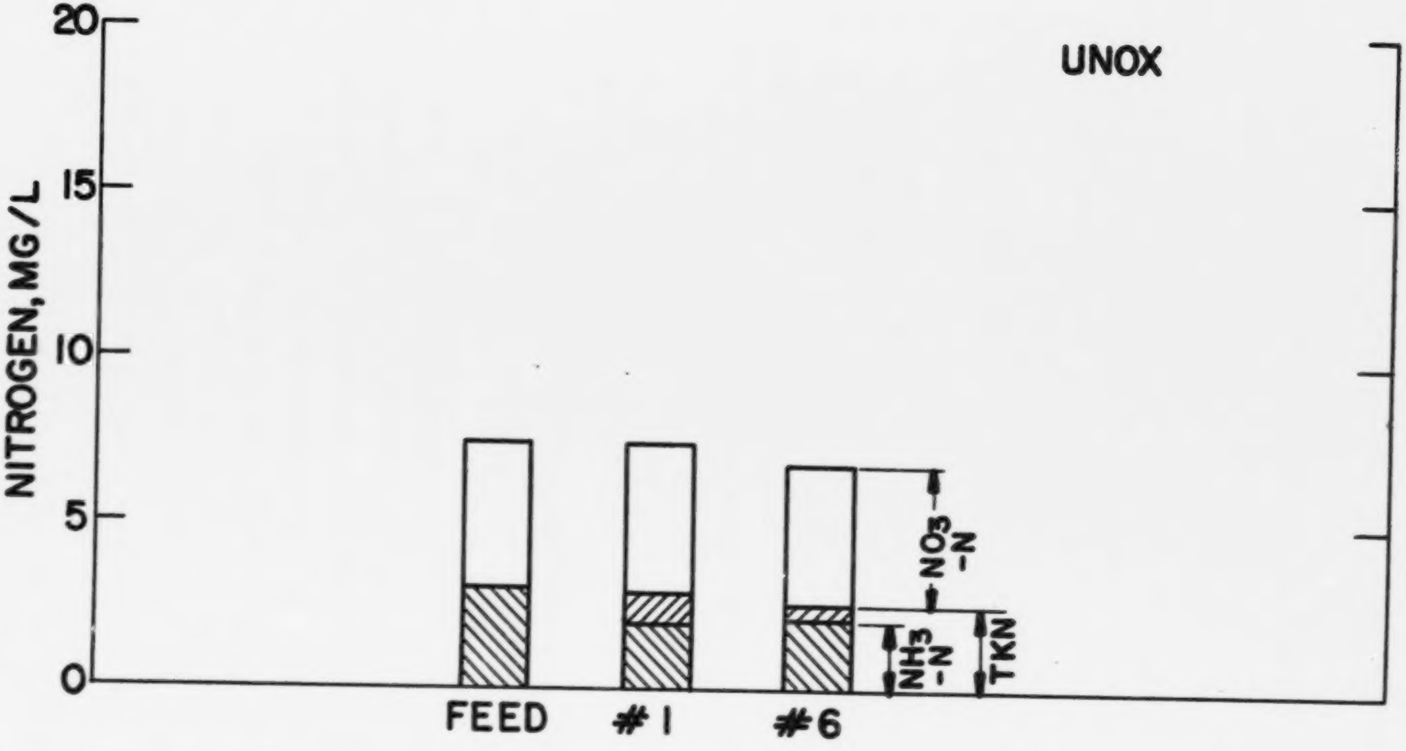

Figure 30. OXIDATION OF NITROGENOUS COMPOUNDS BY OZONE: UN

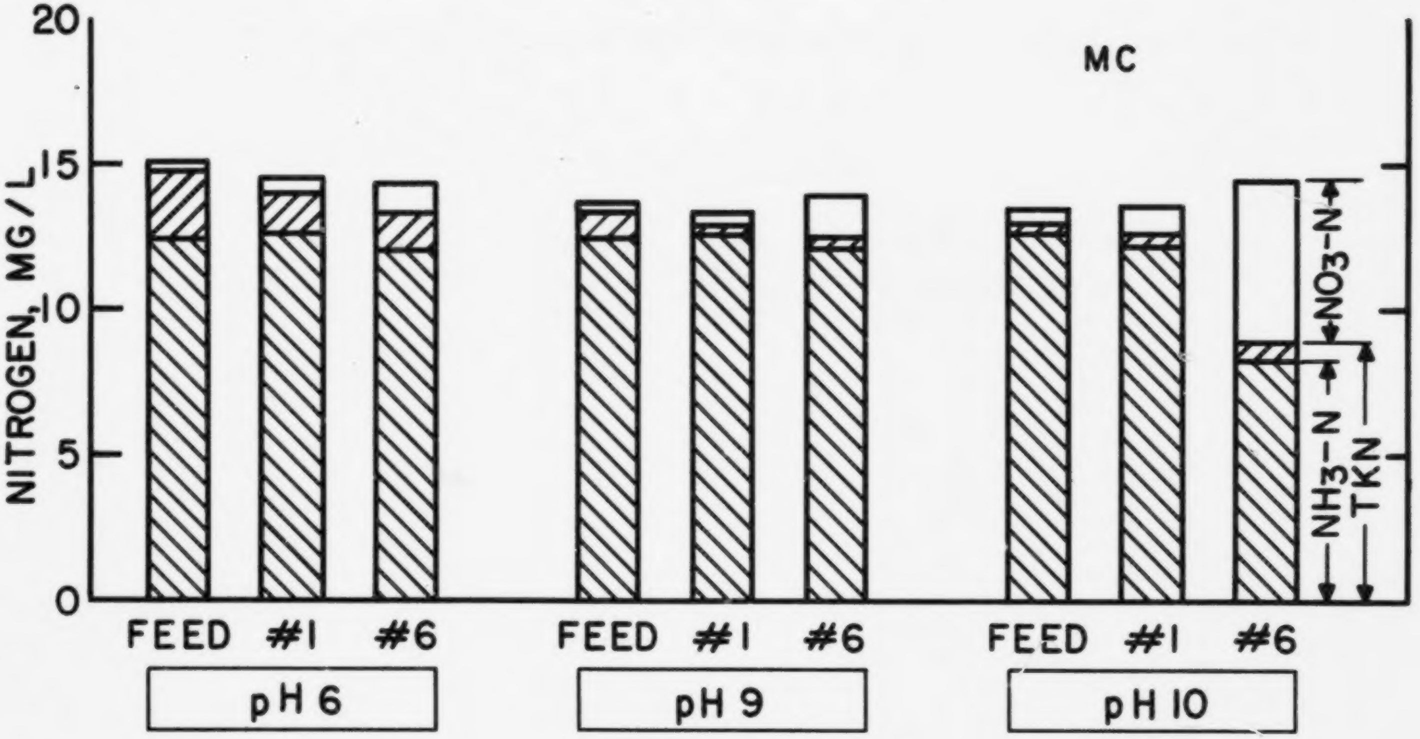

Figure 31. OXIDATION OF NITROGENOUS COMPOUNDS BY OZONE: MC

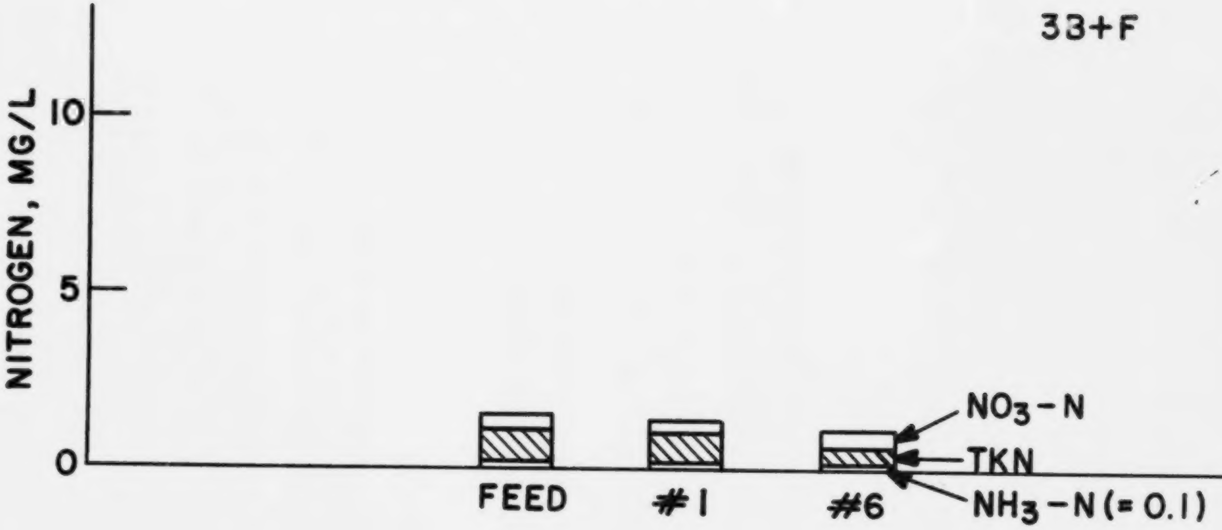

Figure 32. OXIDATION OF NITROGENOUS COMPOUNDS BY OZONE: 3B+F

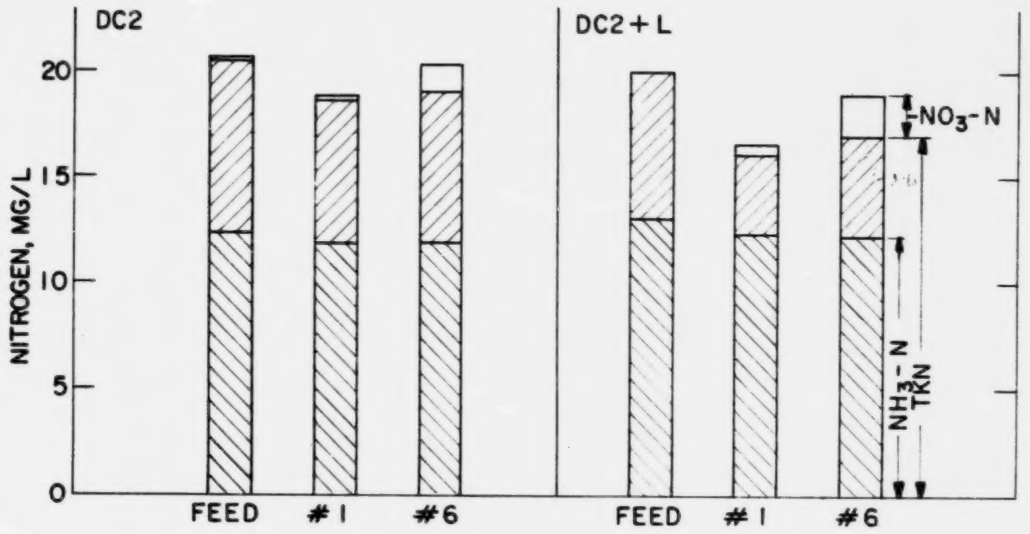

Figure 33. OXIDATION OF NITROGENOUS COMPOUNDS BY OZONE: DC2

3B + F. The three-stage biological process is specifically designed for nitrogen removal. The average data for the 3B + F pretreated feed, illustrated in Fig 32, shows that there was, indeed, very little nitrogen left in this feedwater. Ozone treatment in the pH range 5.4 to 6.9 produced virtually no additional nitrification of the small, residual TKN.

DC2 and DC2 + L. Average results obtained during ozone treatment of the secondary effluent from the main Blue Plains plant, with and without additional lime clarification, are summarized in Fig 33. Both feedwaters had relatively high TKN concentrations and very low nitrate concentrations. Little nitrification by ozone treatment was observed for either feedwater in the pH range 6.9 to 8.1.

Turbidity Reduction

Wastewater turbidity was consistently reduced by ozone treatment. For unfiltered pilot plant feeds, turbidities expressed in Jackson Turbidity Units (JTU) were reduced by about two-thirds during ozone tertiary treatment. In treating filtered feedwaters which had low initial turbidities, product water turbidities of less than one JTU were obtained routinely.

Typical pilot plant data for two unfiltered feedwaters, MC and UN, are illustrated in Fig 34. Feedwater turbidity (circular points) and product water turbidity (triangular points) are shown for a number of runs. The data shown for the MC pretreated feed encompass a pH range 6.1 to 10.9, and those for the UN pretreated feed, a pH range 5.8 to 6.6.

In comparison with the biologically pretreated feed (UN), one might expect a greater portion of the suspended solids in the physicochemical pretreated feed (MC) to be ozone

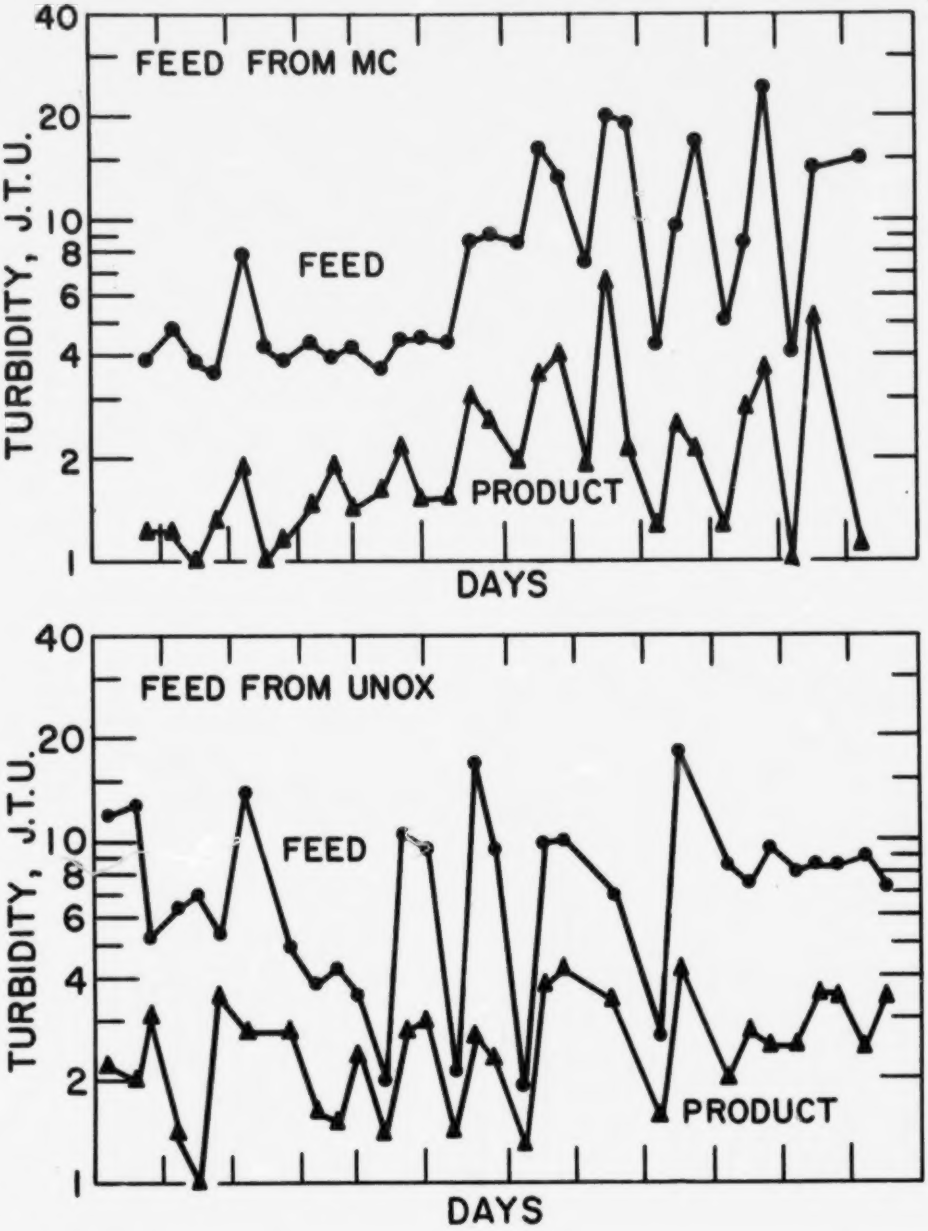

Figure 34. TURBIDITY REDUCTION FOR MC AND UN PRETREATED FEEDS

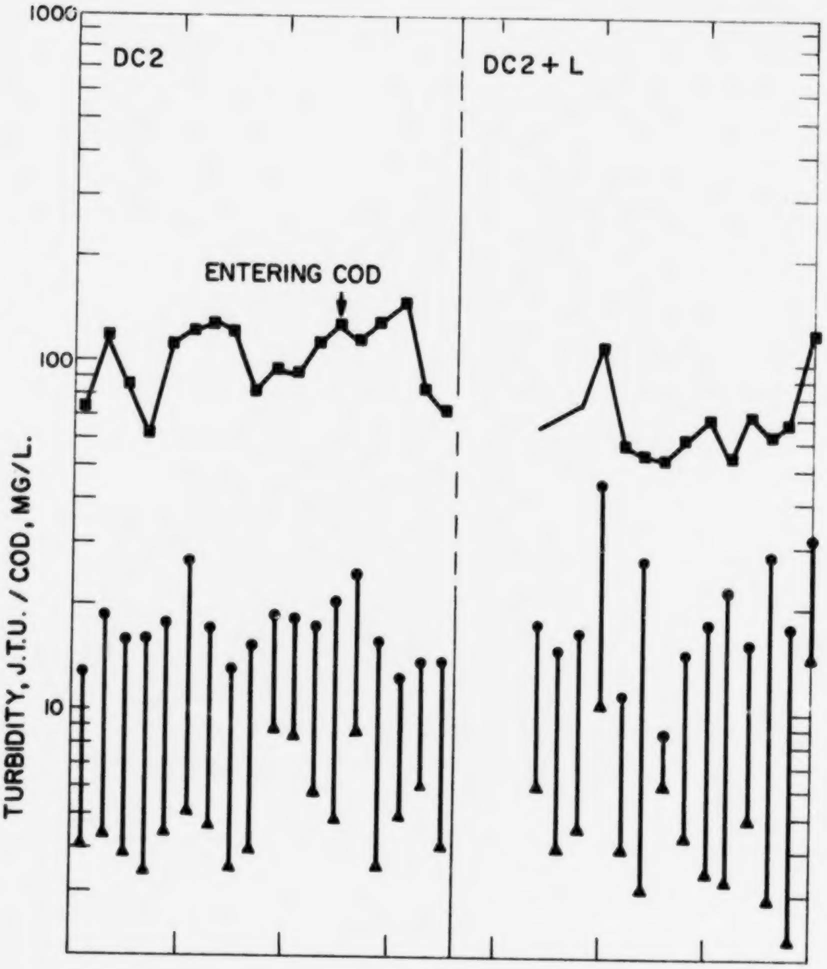

Figure 35. TURBIDITY REDUCTION DURING OZONE TREATMENT OF DC2

resistant inorganic materials, e.g., calcium carbonate. But from Fig 34, it can be seen that the turbidity removal from the MC pretreated feed is, if anything, greater than that from the UN pretreated feed. A possible explanation is an increase in the solubility of suspended inorganic solids due to the pH shift which accompanies ozone tertiary treatment.

A similar graph of turbidity data for the DC2 and DC2 + L feeds is shown in Fig 35 which also includes data for the feedwater COD (square points). It can be seen that the turbidity reductions are, again, quite substantial and that there is little correlation between feedwater COD variations and the turbidity reduction.

Bacteria Kills

During the course of ozone treatment of each type of effluent, samples were taken from four points in the pilot plant for determination of bacteria kill. The points chosen were the neutralization tank and the discharge pipes from the first, third, and sixth reactor stages. The sample systems were thoroughly flushed with the treated water prior to sample collection, and the samples were then drawn into sterile bottles, taking care to avoid contamination during sampling. The samples were taken immediately to the C.W. England Laboratories in Beltsville, Md., so preliminary procedures could be started in about an hour from the time of sampling. Standard plate count, Coliform, and E. Coli were determined on these samples.

Table 8 summarizes the results of these analyses. The No. 1 samples are untreated water and have a substantial total plate count. The wastewater feeds which have been clarified and filtered show lower standard plate counts in the beginning

Table 8.

BACTERIOLOGICAL COUNTS ON WASTEWATER SAMPLES FROM PILOT PLANT

Date of Sample Collection 1971	Type of Wastewater Feed	Sample Point No. & (Treatment Stage)	Standard Plate Count per ml	Coliform Bacteria Most Probable No. per 100 ml	E. Coli Bacteria Most Probable No. per 100 ml
4-28	3B+ L+ F	1 (0)	2,300	46	2.3
		2 (1)	0	<3	<3
		3 (3)	0	<3	<3
		4 (6)	0	<3	<3
5-20	UN+ L+ F	1 (0)	12,000	23	<3
		2 (1)	0	<3	<3
		3 (3)	0	<3	<3
		4 (6)	0	<3	<3
7-9	MC+ CL+ C	1 (0)	110,000	3.6	<3
		2 (1)	0	<3	<3
		3 (3)	0	<3	<3
		4 (6)	0	<3	<3
7-20	MC	1 (0)	150,000	>1,100	<3
		2 (1)	7	<3	<3
		3 (3)	0	<3	<3
		4 (6)	0	<3	<3
8-18	UN[a]	1 (0)	16,000	>1,100	23
		2 (1)[b]	12,000	>1,100	23
		3 (3)	130	<3	<3
		4 (6)	110	<3	<3

Table 8 (Contd)

Date of Sample Collection 1971	Type of Wastewater Feed	Sample Point No. & (Treatment Stage)	Standard Plate Count per ml	Coliform Bacteria Most Probable No. per 100 ml	E. Coli Bacteria Most Probable No. per 100 ml
8-26	MC+CL	1 (0)	12	<3	<3
		2 (1)	8	<3	<3
		3 (3)	14	<3	<3
		4 (6)	74	<3	<3
9-9	3B+F	1 (0)	7,600	>1,100	240
		2 (1)	0	<3	<3
		3 (3)	0	<3	<3
		4 (6)	0	<3	<3
9-17	DC2	1 (0)	54,000	>1,100	9.1
		2 (1)	5	<3	<3
		3 (3)	1	<3	<3
		4 (6)	0	<3	<3
9-30	DC2+L	1 (in)[c]	63,000	>1,100	>1,100
		2 (0)[d]	54,000	>1,100	>1,100
		3 (1)	17	3.6	<3
		4 (3)	1	<3	<3
		5 (6)	0	<3	<3

Notes:
a - Approx. 36 hrs elapsed between sample collection and start of analysis.
b - No ozone was fed to first stage.
c - Sample of District of Columbia secondary wastewater.
d - Sample of District of Columbia secondary wastewater after lime clarification.

and these are reduced to zero in the first ozonation stage.

The mineral clarified, chlorinated and carbon treated (MC+CL+C) effluent had a high plate count indicating that bacteria not only survived chlorination but also multiplied in the carbon column. The bacteria are quickly killed by ozone, however, because the bacteria are not protected by suspended matter.

Other effluents, which had not been filtered, contained more suspended matter as indicated by higher turbidities (4-20 JTU). The standard plate count in these cases did not reduce to zero after the first stage, but usually was reduced to a low value.

To summarize, these tests demonstrate that ozone is a very effective disinfectant for bacteria even in the presence of suspended matter. However, the suspended particles require a longer exposure to obtain a zero standard plate count.

Response to Plant Load Variations

The response of an ozone wastewater treatment plant to variations in load depends entirely upon the details of the plant design. For maximum flexibility, a number of the pilot plant components were intentionally oversized. Therefore, the pilot plant response to load variations is, in itself, of little value for predicting the behavior of a large plant. However, one important point is evident from the pilot plant data: an ozone wastewater treatment plant will respond very rapidly to any load changes. Thus, there is limited surge capacity inherent in the process, but on the other hand, there is no lingering after-effect from large load variations.

A fair approximation of the response of a large ozone wastewater treatment plant to load variations can be calculated from the correlation of dosage data, Eq (11). The necessary assumption is that the plant has a fixed capacity (lb/hr) for dissolving ozone. As is shown in the discussion of economic optimization, below, the dissolution efficiency of the gas-liquid mixers increases slightly with increasing plant load due to the decrease in dissolved ozone concentration (Z). Therefore, the assumption is a conservative one.

As an illustration, again consider the example used in applying the COD correlations for a plant required to reduce COD from 40 mg/l to 20 mg/l. The quantity of ozone to be dissolved was shown to be 0.45 lb ozone/1000 gal feedwater at nominal hydraulic load. Assuming this quantity to be invariant with changes of load, the calculated effects of variations in feed COD (L_f) at constant hydraulic load are shown in Table 9. The calculated effects of hydraulic load variations at constant 40 mg/l COD feed are shown in Table 10.

From Table 9, it can be seen that as the feed COD increases, the product COD (L_p) increases, but in less than direct proportion to the load. At twice the nominal feed COD, a 35% COD reduction is still realized. Recalling that the product water contains about 40 mg/l of dissolved oxygen, the product COD would not exceed the dissolved oxygen content until the COD load exceeded about 165% of nominal load. Up to that point, the product water could exert no net oxygen demand on the receiving stream.

From Table 10, one sees that the percent COD reduction decreases with increasing hydraulic load, but in this example, the product COD would not exceed the dissolved oxygen concentration. Also tabulated is the concentration of ozone dissolved at various hydraulic loadings. The work of others (11) has shown that ozone doses of 7 to 15 mg/l are adequate to meet regulatory disinfection requirements. Thus, even at hydraulic loads of 250% of nominal capacity, this example plant would still have reserve disinfecting capacity.

A practical ozone wastewater treatment plant naturally would incorporate provisions for meeting normal load variations. But even in this restricted example of a completely inflexible plant, relatively large overloads are seen to produce neither health nor ecological hazards.

Summary

The anticipated technical virtues of ozone wastewater treatment were all demonstrated in the pilot plant. COD, turbidity, and surfactants were significantly reduced, and the product water was nearer neutral pH, oxygen saturated, and practically free of bacteria. No extraneous chemical additives remained in the water, and there were no residual materials to be disposed of.

For domestic wastewater similar to that at Blue Plains, the relations between L_f, L_p, pH, t*, Z* and D* can be estimated from the correlations shown in this section.

Table 9.

RESPONSE TO CHANGE IN FEED COD AT CONSTANT HYDRAULIC LOAD OF A PLANT CAPABLE OF DISSOLVING 0.45 LB OZONE/1000 GAL FEEDWATER

Load Factor	L_f mg/l	L_p mg/l	% COD Reduction
0.50	20	6.9	65.4
0.75	30	13.0	56.5
1.00	40	20.0	50.0
1.25	50	27.6	44.9
1.50	60	35.4	41.0
2.00	80	52.1	34.9
2.50	100	69.5	30.5

Table 10.

RESPONSE TO CHANGES IN HYDRAULIC LOAD AT CONSTANT L_f = 40 mg/l OF A PLANT CAPABLE OF DISSOLVING 0.45 lb OF OZONE PER 1000 GAL FEEDWATER

Hydraulic Load Factor	L_p mg/l	% COD Reduction	mg/l Ozone Dissolved
0.50	10.0	75.0	108.0
0.75	15.9	60.3	72.0
1.00	20.0	50.0	54.0
1.25	23.0	42.5	43.2
1.50	25.0	37.0	36.0
2.00	28.3	29.3	27.0
2.50	30.3	24.2	21.6

SECTION VIII

CHARACTERISTICS OF PILOT PLANT EQUIPMENT

Having at this point described and discussed the technical results obtained from the ozone wastewater treatment process, the next major consideration is the projected costs for large plants. Since these cost projections will be based largely on scaling-up the pilot plant process, it is necessary to first describe and correlate the performance of several pieces of the pilot plant equipment.

Ozone Generator

The ozone generator used in the pilot plant was a commercial, 34 tube unit which is further described in Appendix 2. In the first few months of operation, the individual fuses to four of the thirty-four tubes opened. This is said to be expected on initial start-up, and that upon replacement of the weak glass dielectric tubes, very few additional failures should be expected. However, the four tubes were not replaced because the machine still slightly exceeded the manufacturer's performance specifications, and the unit operated reliability and without further incident for the remainder of the nine-month pilot plant operation.

The electric power consumption of the ozone generator is a major part of the total ozone water treatment cost. For power measurements, the generator was supplied with an ammeter, voltmeter, and electrodynamometer kilowatt meter connected between the variable transformers and the high voltage transformer. Data from these three instruments were recorded for all plant runs.

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The treatment of the MC pretreated feed, which had a moderately high COD, offered the first opportunity for operating the ozone generator at high power inputs. It then became apparent that the calculated generator efficiencies were uncommonly high and the power factors suspiciously low. Recognizing that the highly distorted a.c. wave forms produced by the ozone generator could easily introduce errors into the power measurements, a check on the accuracy of the electrodynamometer kilowatt meter was made.

The physically accurate measurement of very distorted a.c. power is difficult. But from the engineering viewpoint, physical accuracy is not so necessary as is economic accuracy: the practically important engineering parameter is the cost of power for operating the ozone generator. It was, therefore, decided to check the indicating kilowatt meter against the type of meter commonly used for utility billing purposes, namely, an induction watt-hour meter.

A commercial watt-hour meter with the necessary matching transformer was loaned for this purpose by the Potomac Electric Power Co. (PEPCO). This instrument was connected to the ozone generator, and a series of calibrations were made covering the full range of electrical power inputs and gas flows. It was found that the electrodynamometer kilowatt meter was, indeed, reading low, especially at higher powers. (At the same time, tests were made to confirm that the losses in the variable transformers were negligibly small.)

On the basis of this calibration, it was found that at lower power inputs, the relation between the two meters was as follows:

$$Kw_p = 1.537\ (Kw_w) - 0.0607\ (Kw_w)^2 + 0.0025\ (Kw_w)^{3.661} \quad (15)$$

where Kw_p is the reading from the induction watt-hour meter, and

Kw_w is the reading from the electrodynamcmeter kilowatt meter.

However, above Kw_w readings of about 5 Kw, the electrodynamometer instrument responded little to further increases of power.

From the voltmeter and the ammeter readings, the Kva could be compared with the induction watt-hour meter. It was found that over the range 1 to 10 Kw input, the following relation existed.

$$Kw_p = 0.748\ (Kva) - 0.00619\ (Kva)^{2.153} \qquad (16)$$

For both Eq (15) and Eq (16), no significant effects of gas flow rate were observed. Many comparisons of the several instruments during subsequent plant operations verified the original calibrations which are estimated to be precise within about ten percent.

Since only data from the ammeter, voltmeter, and electrodynamometer kilowatt meter had been collected during the earlier plant operations, this procedure was continued, and all of the power data was then converted to the induction watthour meter basis according to Eq (15) and Eq (16). Both the ammeter and voltmeter had nonlinear scales which precluded precise readings at low powers. Therefore, Eq (15) was used for Kw_w values up to 4.3 Kw, and Eq (16) was used for the higher power inputs.

On the basis of the corrected power inputs, the efficiency of the ozone generator, Kwh/lb O_3, was computed for all of the plant runs from February through September. The average efficiencies of the generator during that period are shown in Figure 36. These curves offer a realistic description

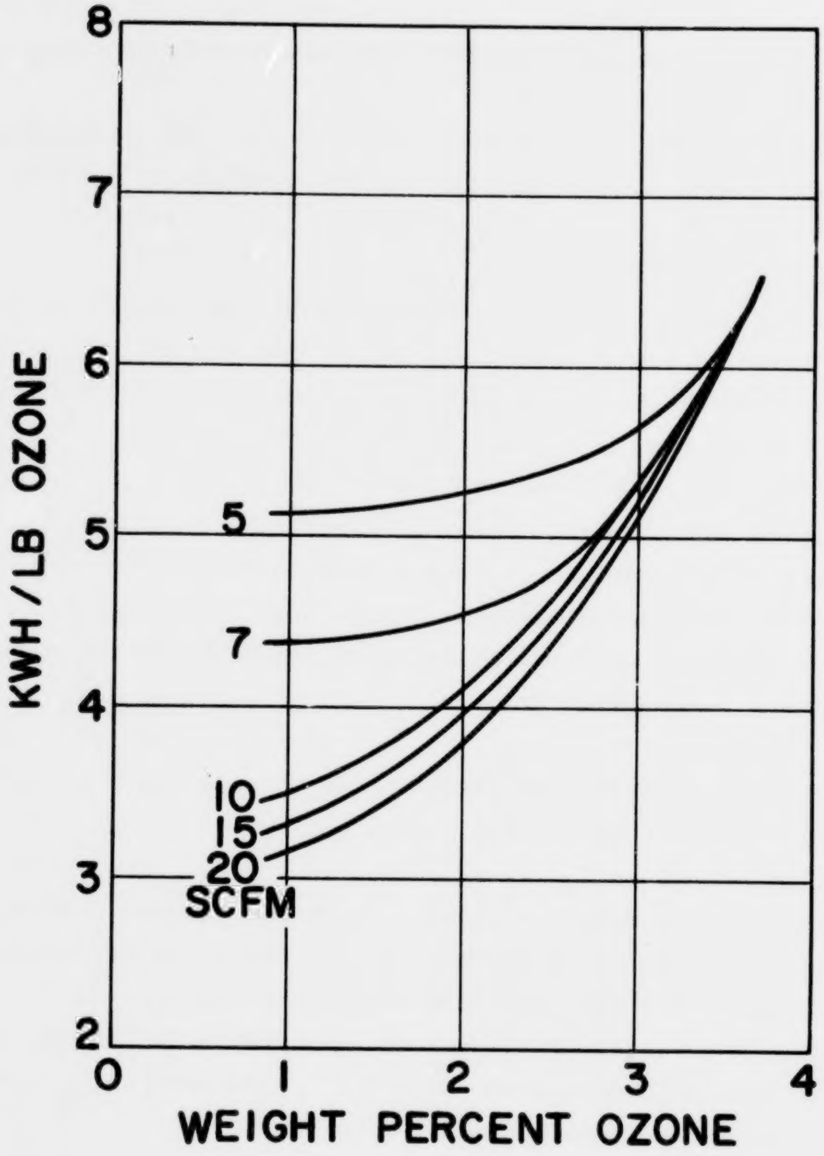

Figure 36. AVERAGE EFFICIENCY OF PILOT PLANT OZONE GENERATOR

of the performance that can be expected from this type of ozone generator in practical plant operations, including as it does, the effects of less than perfect maintenance.

Gas-Liquid Mixers

General. In the ozone treatment of wastewater, the ozone must be dissolved from the gas into the wastewater before any reaction with contaminants can occur. Since ozone can be safely and economically produced only in relatively low concentrations, and since the cost of ozone production is a major part of the total cost of ozone treatment, highly effective gas-liquid mixing equipment is necessary for dissolving the ozone.

In the tertiary treatment of wastewater, the required ozone dosage is comparatively high. In many practical cases, the volume of ozone gas mixtures handled is roughly the same as the volume of water treated. Mixing devices suited to roughly equal volumetric flows of gas and liquid are not common. The prepilot development of the mixing devices used in the ozone pilot plant is described in Appendix 1.

Each of the six reactors in the ozone pilot plant incorporated identical mixing devices. A typical mixer is shown schematically in Figure 37. Water is forced through the nozzle of an eductor atop each reactor where it is mixed with the ozone bearing gas. The dispersed gas in liquid stream immediately enters a high-shear zone where it is impinged by jets of additional water. The turbulent dispersion is then forced down a 4-inch ID dissolver tube to near the bottom of the reactor. There, a cap distributes the flow evenly in the reactor cross-section, and the gas bubbles are allowed to ascend through the water in the reactor.

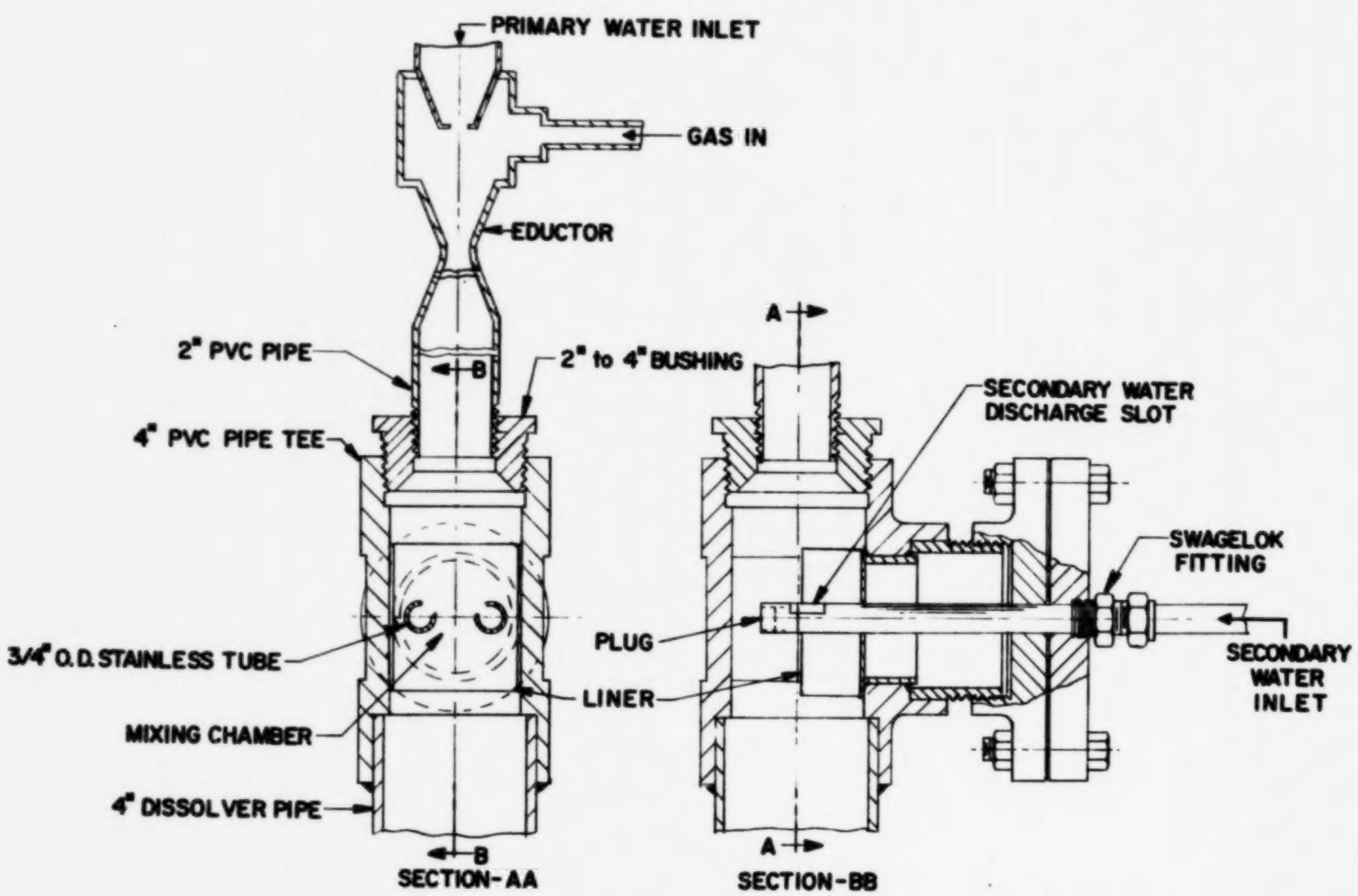
PRIMARY WATER INLET
GAS IN
EDUCTOR
2" PVC PIPE
B
2" to 4" BUSHING
4" PVC PIPE TEE
3/4" O.D. STAINLESS TUBE
MIXING CHAMBER
LINER
4" DISSOLVER PIPE
SECTION-AA
A
SECONDARY WATER DISCHARGE SLOT
PLUG
SWAGELOK FITTING
SECONDARY WATER INLET
SECTION-BB

Figure 37. SCHEMATIC OF PILOT PLANT MIXER ASSEMBLY

The water and gas feeds to each mixer were manually adjusted and were individually metered. Water feed is supplied by a separate pump for each mixer. Each pump, except the first, draws from a line connecting the outlet of the preceding reactor to the bottom of the reactor it feeds. Thereby, the water flow through a mixer does not have to be matched to the feedwater flow. If mixer water flow is greater than the feedwater flow, part of the water to the mixer is recycled from the bottom of the reactor. Conversely, if the mixer flow is less than the feedwater flow, part of the overflow from the preceding reactor does not pass through the mixer, but is bypassed directly into the bottom of the reactor.

Definition of Mixer Performance: Transference (T). The processes occuring in the pilot plant mixers are complicated. There are four separate zones of mixing; first, in the eductor, then in the high turbulence zone immediately below the eductor, then in the dissolver tube and, finally, in the reactor itself. And this complexity is compounded by concurrent chemical reaction. A detailed analysis of all of these simultaneous and interrelated processes would obviously be hopelessly complex. The alternative is to make bold, but well defined, simplifying assumptions. Such has been done.

The combined mixer and reactor are considered to be a "black box" cocurrent mixer. Gas and water flows at the inlet and outlet and the ozone concentrations in each stream are experimentally known, but nothing is known or assumed about ozone concentrations anywhere within the mixer-reactor unit. To this "black box" model a basic form of rate equation is then applied: mass flux equals a conductance factor times an average driving force. For cocurrent processes, it is known that the log mean average is the generally applicable averaging procedure for the driving force. The mass flux, Q, is expressed as lb ozone dissolved/hour, and the driving force as atmospheres ozone partial pressure. Lacking a more specific term, the conductance factor will here be called transference (lb ozone dissolved/hr/atm average ozone partial pressure driving force), and it will be assigned the symbol T.

$$T = Q/\Delta p_m \tag{17}$$

where Δp_m is the log mean average of the difference in ozone partial pressures in the gas and in the liquid, at the mixer inlet and the reactor outlet, in atmospheres.

At the mixer inlet of the i-th reactor, the partial pressure driving force, Δp_1, is as follows:

$$\Delta p_1 = P_1 v_g - Z_{i-1}/H \tag{18}$$

where P_1 is absolute gas pressure, atm

v_g is the volume fraction ozone in the gas from the generator

Z_{i-1} is the dissolved ozone concentration from the outlet of the preceding reactor

H is Henry's Law solubility constant for ozone mg/l/atm

The relation between volume fraction and wt percent ozone in oxygen is $v = 2c/(300-c)$, or to a good approximation for small values of c, $v = 0.00667c$.

Similarly, the partial pressure driving force, Δp_2, at the outlet of the reactor, is as follows:

$$\Delta p_2 = P_2 v_v - Z_i/H \tag{19}$$

where P_2 is the absolute pressure in the ullage of the reactor (suction pressure of the recycle gas compressor), atm

v_v is the volume fraction ozone left in the spent gas

Z_i is the dissolved ozone concentration at the outlet of the i-th reactor

The log mean average is defined as follows:

$$\Delta p_m = (\Delta p_1 - \Delta p_2)/\mathrm{Ln}(\Delta p_1/\Delta p_2) \qquad (20)$$

In writing the expression for Δp_m in terms of experimentally measured variables, one small simplifying assumption can be made immediately, namely, $Z_{i-1} = Z_i$. This assumption has no effect on Δp_2, and because the ozone partial pressure in the gas is very much larger than that in the liquid at the mixer inlet, the effect on Δp_1 is negligibly small. It will also be convenient to express $P_1 = P_2\ (1+d)$. Also for convenience, the relation between v_g and v_v can be expressed in terms of the fraction of the ozone feed dissolved, f.

$$f = (v_g - v_v)/v_g \qquad (21)$$

Combining Eq (18), (19), (20), and (21), the log mean ozone partial pressure driving force for the i-th mixer-reactor combination is as follows:

$$\Delta p_m = \frac{P_2 v_g (d+f)}{\mathrm{Ln}[(HP_2 v_g (1+d) - Z_i)/(HP_2 v_g (1-f) - Z_i)]} \qquad (22)$$

For calculating T from Eq (17), Q can be easily calculated from the experimental gas flow and concentration data. In Eq (22), the value of d corresponds to the hydrostatic head of about half the submerged depth of the dissolver tube, eight feet. Since P_2 is about 2 psig, d is about 0.21. The only variable in the Eq (22) for calculating Δp_m that is not available from the plant data is the solubility constant, H.

Solubility and Half-Life of Ozone in Wastewater. Among the objectives of the post-ozonation experiment was the direct determination of ozone solubility in wastewater and the rate that dissolved ozone disappears by the combined processes of reaction with COD and autodecomposition. There appear to be no published data for these properties. In fact, the published data for the solubility of ozone in pure water are somewhat discordant.

Two sets of published data for the solubility of ozone in pure water, designated G(14) and M(15) are shown in Fig 38. Also shown as solid circles are points measured for distilled water at 25°C in the post-ozonation apparatus which demonstrate that the solubility measurements are reasonably reproducible for pure water. For comparison purposes, the short curve segment, A, has been drawn through the average of the four experimental points and approximately parallel to the published curves.

The rate at which dissolved ozone disappears from water can be approximated by a first-order reaction.

$$\mathrm{Ln}(Z/Z_o) = -k_Z t \qquad (23)$$

For these kinetics, the reaction can be characterized by a dissolved ozone half-life which is often easier to conceptually relate to actual processes than is the value of k_Z. At any point in the reaction, half the remaining dissolved ozone will disappear in one half-life, three-quarters in two half-lives, seven-eights in three half-lives, etc.

Half-life values for dissolved ozone obtained from the post-ozonation apparatus for several different feeds (which are defined in Table 2) and for distilled water are shown in Figure 39 as a function of the COD remaining at the end of the post-ozonation experiment. The data scatter rather badly. This may possibly be caused by variation in dissolved salt concentration, residual suspended solids, pH, etc. Nevertheless, there is a clear trend for the half-life to increase with decreasing residual COD. These data offer some guide as to how long it will take for residual dissolved ozone to disappear from the product water after ozone treatment.

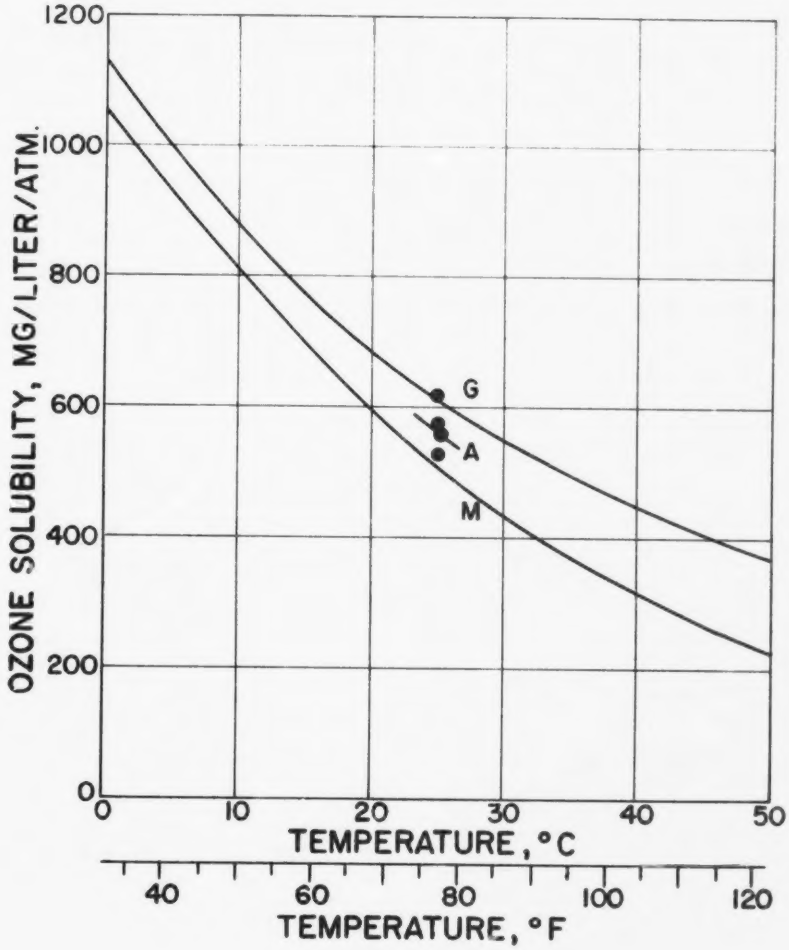

Figure 38. SOLUBILITIES OF OZONE IN PURE WATER

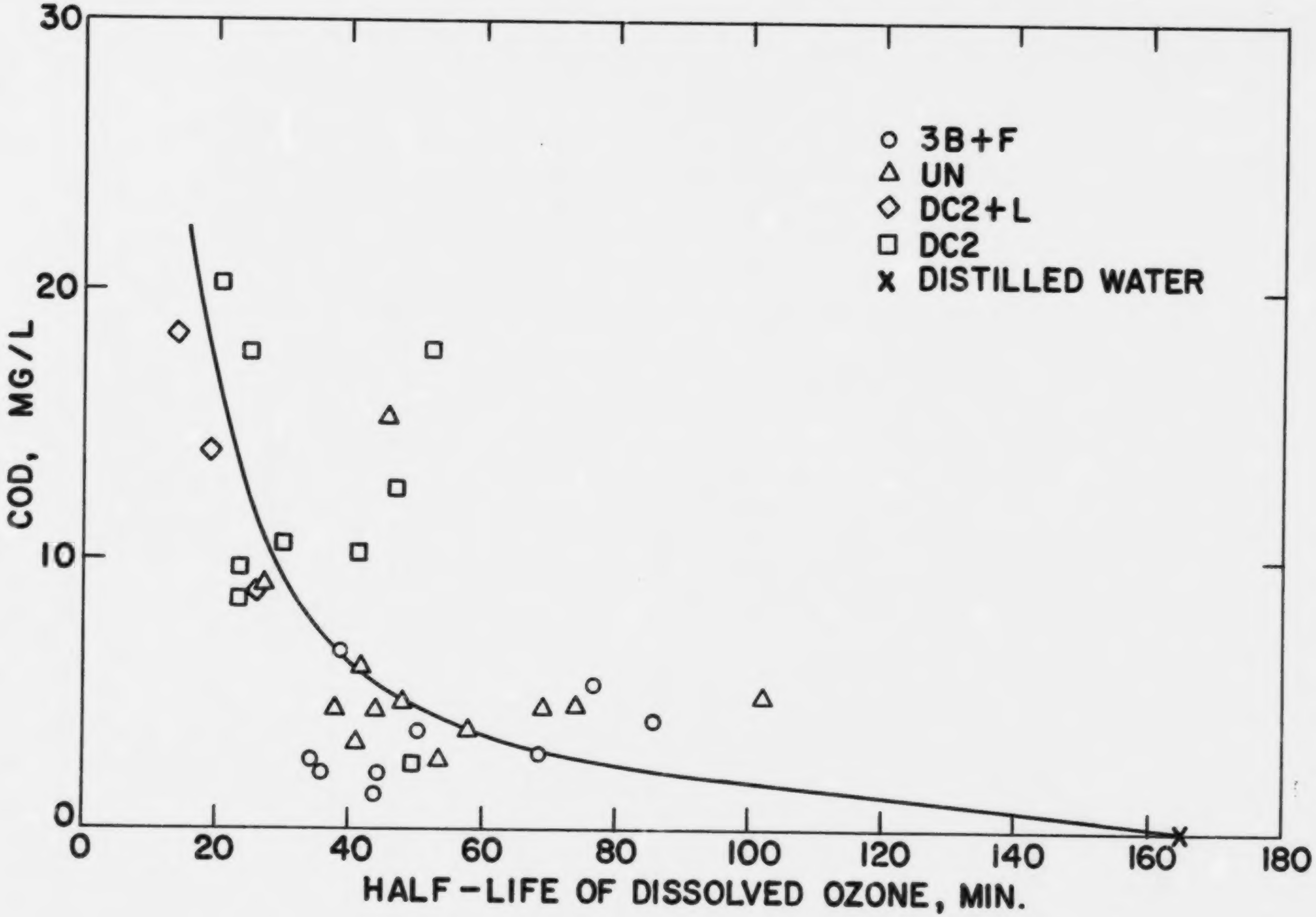

Figure 39. RELATION BETWEEN OZONE HALF-LIFE AND COD REMAINING IN WATER

The data for ozone solubility in well treated wastewater obtained from the post-ozonation apparatus are also scattered. But taken at their face value, they suggest that ozone solubility decreases with increasing residual COD. This is perhaps real, but much more likely, it indicates mass transfer limitations in these experiments; i.e., the dissolved ozone was being consumed at a rate comparable to the dissolution rate from the gas. (However, before starting routine operation of the post-ozonation apparatus, tests were made on relatively low COD product water (UN) using several rates of ozone gas sparging. No correlation between the measured solubility and the rate of ozone sparging was observed, indicating that there was no mass transfer limitation.)

Since the half-life of dissolved ozone determined in each experiment is a measure of the actual rate of ozone consumption, the ozone solubility in the absence of any ozone consumption, and hence in the absence of any mass transfer limitation, can be estimated by extrapolating the experimental data to the limit of infinite dissolved ozone half-life. Such extrapolations are commonly accomplished using reciprocal plots: extrapolating the reciprocal of a variable to zero is equivalent to extrapolating the variable to infinity.

Ozone solubility in wastewater, expressed as percent of the measured solubility in distilled water at the same temperature, is plotted against the reciprocal dissolved ozone half-life in Fig 40. Each point represents one run in the post-ozonation apparatus, and points are included for wastewaters subjected to several different pretreatments (see Table 2).

The scatter of these data is such that several interpretations

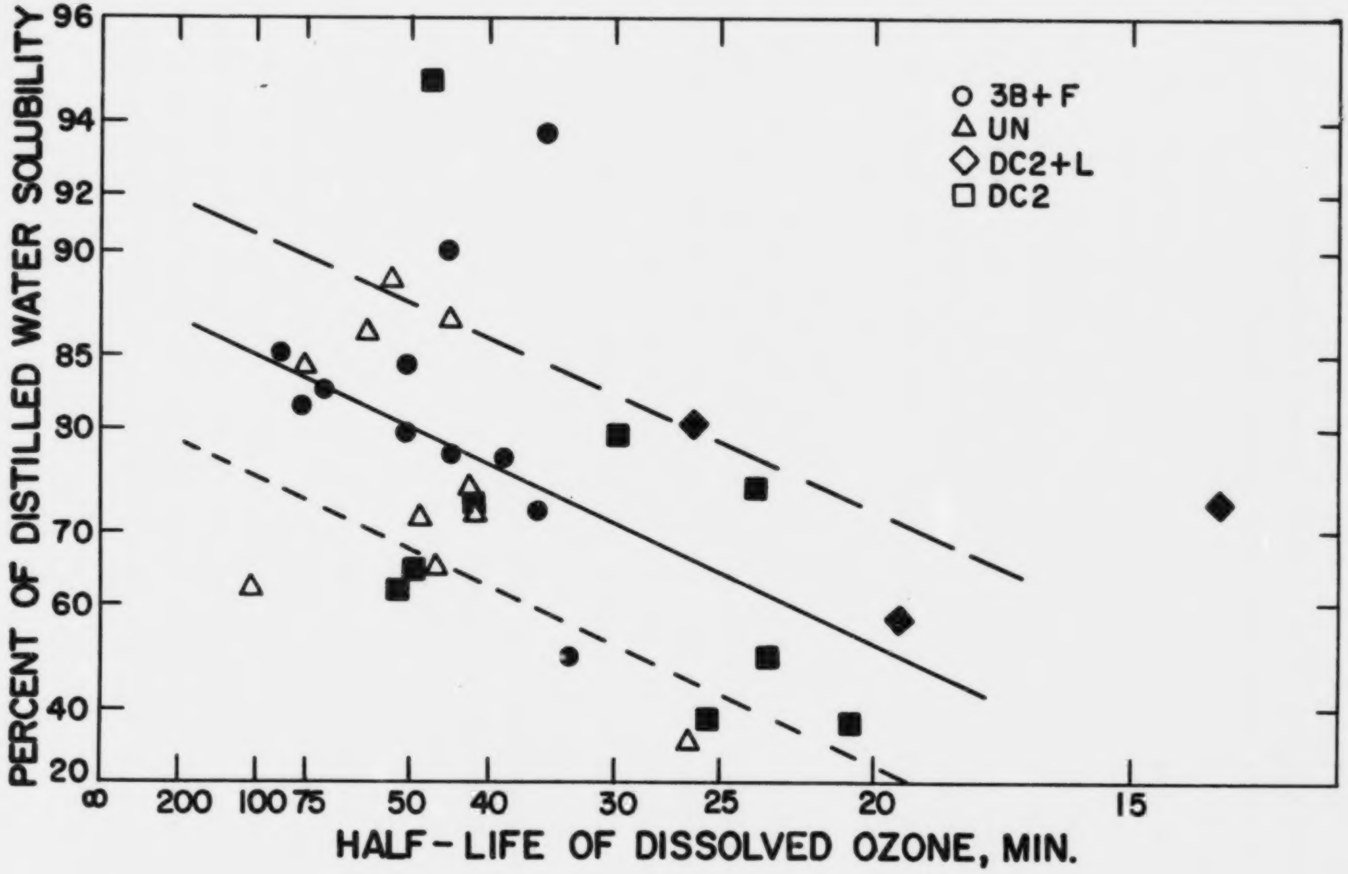

Figure 40. OZONE SOLUBILITY IN WATER vs RECIPROCAL HALF-LIFE

are possible. A straight line bracketed by dashed lines approximating the scatter limits has been drawn through the data in Fig 40. Extrapolation to zero reciprocal half-life indicates a solubility in the range 80 to 93 percent of that in distilled water. However, one can equally well interpret these scattered data as showing no significant dependence of solubility on half-life for half-lives greater than about 30 minutes.

Assuming that there are no gross sampling or analytical errors reflected in these data, it appears that the solubility of ozone in well-treated wastewater must depend on other variables besides dissolved ozone half-life and temperature. Other possible variables are dissolved salt concentrations, suspended solids, and small differences in pH. But from the fall of the experimental data, the average solubility appears to be generally within the range 70% to 90% of the solubility in pure water.

From these data and from some results of the mixer performance correlation described below, the solubility of ozone in these wastewaters was assumed to be 85% of the distilled water solubility, i.e., 541 mg/l/atm at 70° F.

Correlation of Mixer Performance. Having selected a value for solubility, sufficient data were available for calculating transference of the mixers from plant data. Values of T were computed using Eq (17), (18), (19) and (20) with one additional refinement. When the water flow through a mixer was greater than the feedwater flow, it was a combination of the outlet from the preceding reactor and water recycled from the bottom of the reactor. Since in these cases Z data were available for both streams, the value of Z_{i-1} in Eq (18) was adjusted accordingly; the correction was very small.

Most of the time, the mixers in the pilot plant were operated at one of three water flows, about 20, 35, and 55 gpm. Dividing the applicable part of the plant mixer data into these three flow groups, the values of T and the mechanical work consumed by each mixer were computed. Because of the suspect accuracy of the dissolved ozone analyses made prior to 6/24/71, only plant data collected after that date were used. Because of the masking effect of available chlorine on the dissolved ozone analyses, the data for the MC+CL pretreated feedwater were not used. No estimated values for dissolved ozone concentrations or spent gas compositions were used. Mechanical work was calculated from stream flows and pressure drops assuming pump and adiabatic compression efficiencies of 70 percent. Compressor work was taken as that necessary to compress the gas from the pressure in the reactor ullage to that at the mixer inlet.

Examination of the data showed that, on log-log coordinates, values of T and mixer efficiency, transference/KW mechanical work, fell along a straight line. Lines fitted by least squares to each of the three flow groups, together with the experimental points for the 35 gpm group, are shown in Figure 41. Although not separately symbolized, the data points include data for different feeds, pH, and mixers. Clearly all data fall on a line, and they do not scatter too badly. The three fitted lines suggest that at constant efficiency, the transference is proportional to the flow rate. And, it is evident that mixer efficiency increases with increasing transference.

As a matter of additional interest, a zero gpm line is shown which was determined from a few runs made on UN feed in which gas was simply blown down the dissolver tube and allowed to ascend through the reactor as large, irregularly shaped bubbles. While comparatively little mechanical work was consumed, the transferences were very low.

The least-square fitting of the data for the three flow groups was conducted using a number of assumed solubility values. The overall best fits were obtained using values of H in the 520 to 560 mg/l/atm range. This was one of the reasons for selecting the 85% of distilled water value for H. Fits were even tried with the assumption that H varied with COD; however, the improvement in fit was negligibly small.

On the basis of the data for the three flow groups, all of the T vs T/KW data were fit to the following expression using about the same modified multiple regression procedure described above for obtaining Eq (12).

$$\mathrm{Ln}\ T = a_o + a_1 \mathrm{Ln}(T/KW) + a_2 W_m \qquad (24)$$

where W_m is the water flow to the mixer, gpm

$a_o = -3.558 \pm 0.062$

$a_1 = 1.232 \pm 0.013$

$a_2 = 0.03899 \pm 0.00054$

The coefficient values represent a fit to 636 data points after discarding 12 "wild" points, and the indicated uncertainties represent one standard deviation. The standard sample deviation in Ln T is 0.153, indicating that the data scatter 16% about the fitted value of T.

The effects of gas flow rates on mixer performance must also be correlated. Rather than using gas flow directly, the gas to liquid volumetric ratio, G/L (SCF gas/CF water) was used as the correlating parameter.

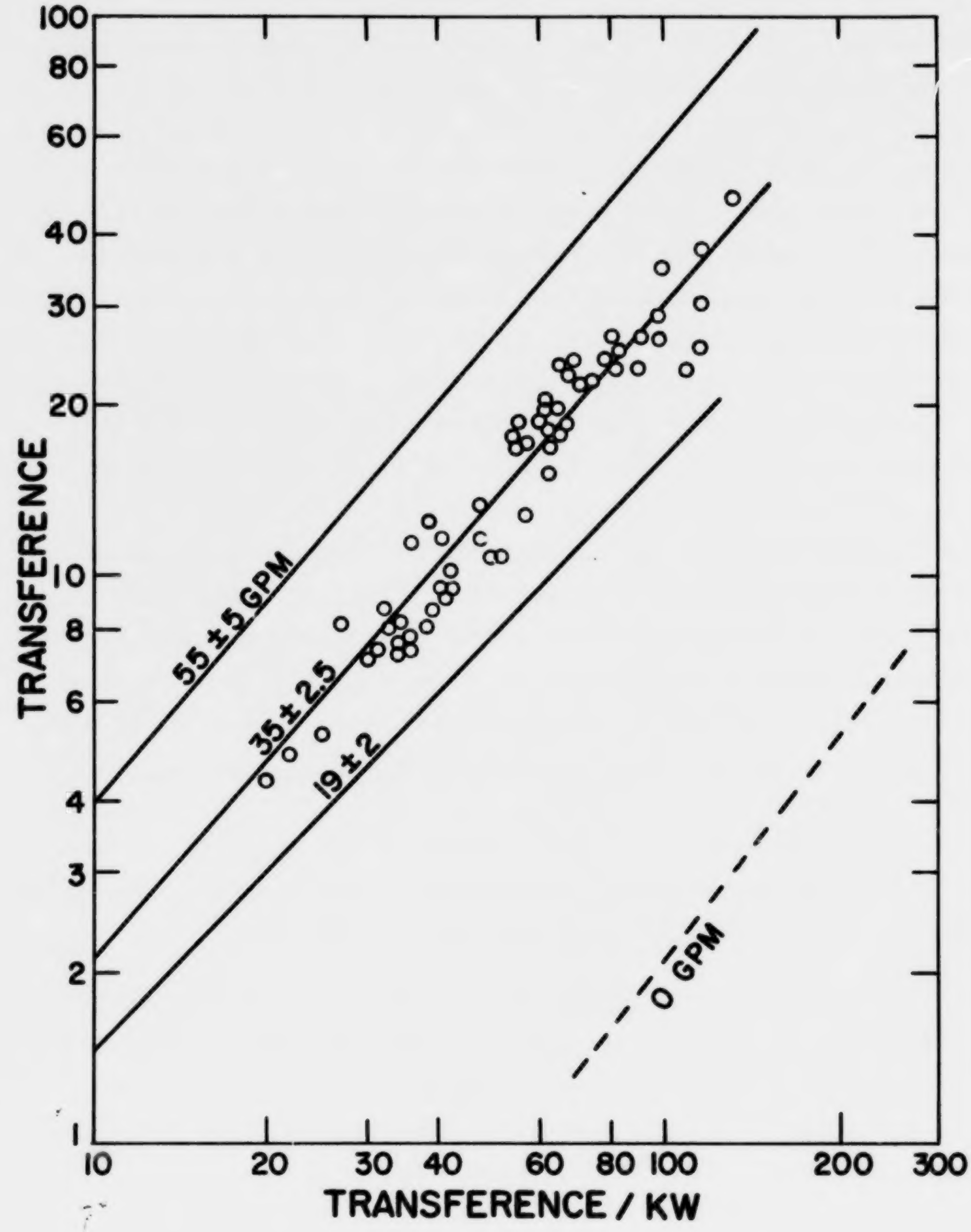

Figure 41. PILOT PLANT MIXER TRANSFERENCE (T) vs MECHANICAL EFFICIENCY (T/KW) FOR VARIOUS WATER FLOW RATES

Again grouping the data into three groups according to water flow, values for T and G/L were computed for each mixer from raw plant data. These values are plotted in Figure 42 on log-log coordinates for the 20 and 55 gpm flow groups. These T vs G/L data exhibit considerable scattering. Part is due, no doubt, to experimental error, but one might suspect that variation in water properties, notably surface tension variations caused by surfactants, could also be responsible for part of the scattering.

In any event, the data for 20 gpm fall pretty much along a straight line. The 35 gpm data (not shown) do likewise. But the 55 gpm data show a very pronounced curvature. No other plotting coordinates were found which would make all of the flow groups linear and also satisfy the physical requirement that T approach zero as G/L approaches zero. Thus, any correlating function fitting all of the data must contain a term strongly nonlinear in W_m.

A number of correlating functions were examined using the modified multiple regression procedure. The most reasonable fit was obtained with the following equation.

$$\mathrm{Ln}\,T = a_o + a_1 W_m + a_2 \mathrm{Ln}(G/L) + a_3 W_m{}^3 (G/L) \qquad (25)$$

where $a_o = 2.478 \pm 0.050$

$a_1 = 0.0122 \pm 0.0022$

$a_2 = 0.4888 \pm 0.0270$

$a_3 = 0.0000526 \pm 0.0000066$

The coefficient values represent a fit to 638 data points after discarding 10 "wild" points, and the indicated uncertainties represent one standard deviation. The standard sample deviation in Ln T is 0.306, indicating that the data scatter 36% about the fitted value of T. The curves for

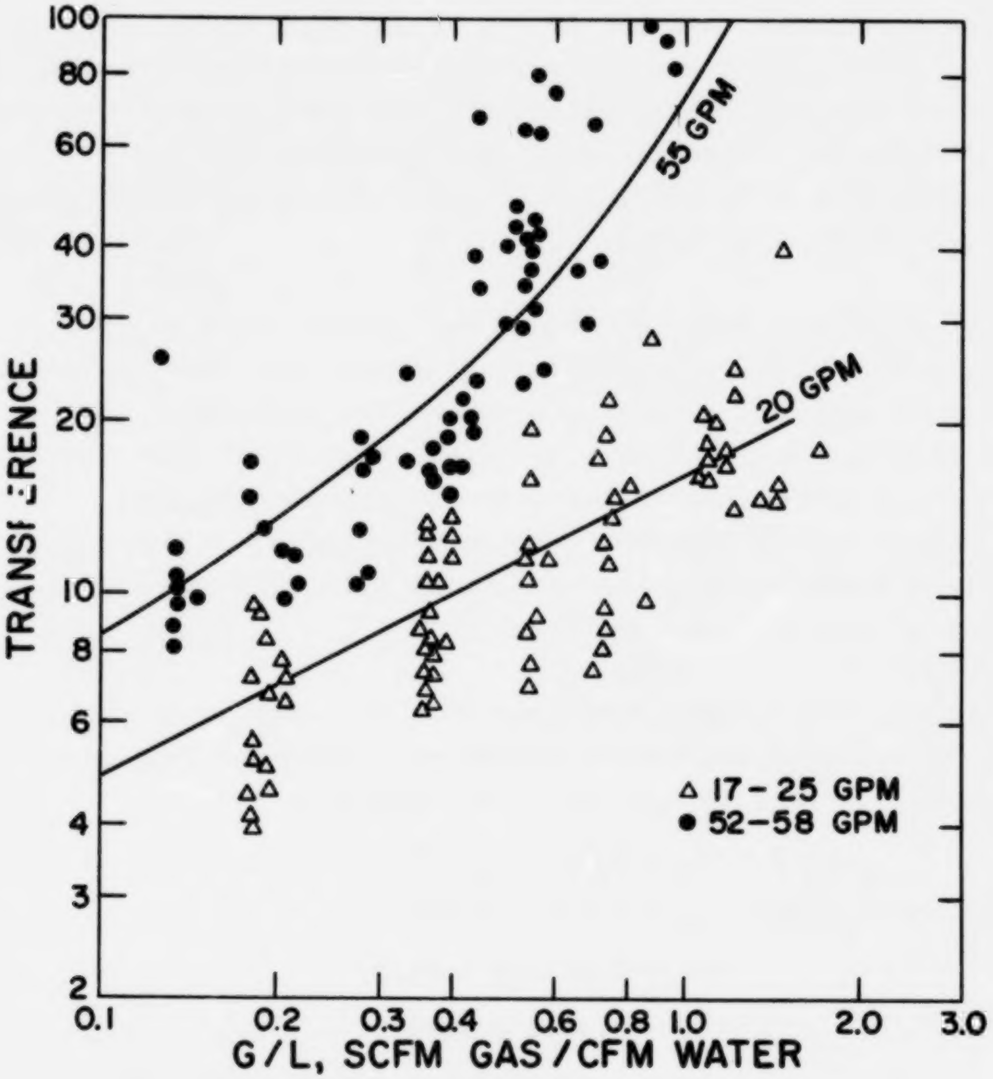

Figure 42. PILOT PLANT MIXER TRANSFERENCE (T) vs GAS TO LIQUID VOLUME RATIO (G/L) FOR TWO WATER FLOW RATES

20 and 55 gpm in Figure 42 represent Eq (25).

Equations (24) and (25) constitute a complete correlation of the mixer performance based on the pilot plant data. These two equations are shown graphically in Figure 43. From Figure 43, it is evident that maximum transference and maximum mixer efficiency are attained at the highest G/L values. But, in the prepilot testing of the mixers, it was found that when G/L was increased much above one, the mixers tended to become hydraulically unstable. At a G/L value of about one, the transference increases with increasing water flow, at least up to the approximately 55 gpm maximum examined in the pilot plant. And at G/L=1, the mixer efficiency is nearly independent of flow rate; transference is directly proportional to the mechanical power expended.

Practically, it can be concluded that optimum mixer performance occurs at G/L=1, and the maximum transference verified by extensive plant data is obtained at water flow of 55 gpm. Under these conditions, a transference of about 80 can be expected with a T/KW of about 110.

Vacuum Deaerator

The vacuum deaerator consisted of a 120 gallon cylindrical vacuum chamber 30 in. in diameter by 36 in. high. The water entered through a spray nozzle in the middle of the head. The vacuum connection was concentric with the spray nozzle. Vacuum was produced by a 1 h.p., single stage, liquid-ring vacuum pump rated for 6.5 cfm at 27 in. mercury vacuum. The maximum amount of gas coming out of the water at 27 in. Hg vacuum is 2.3 cfm at 60 gpm feed rate.

Water level was maintained near the bottom of the tank by a

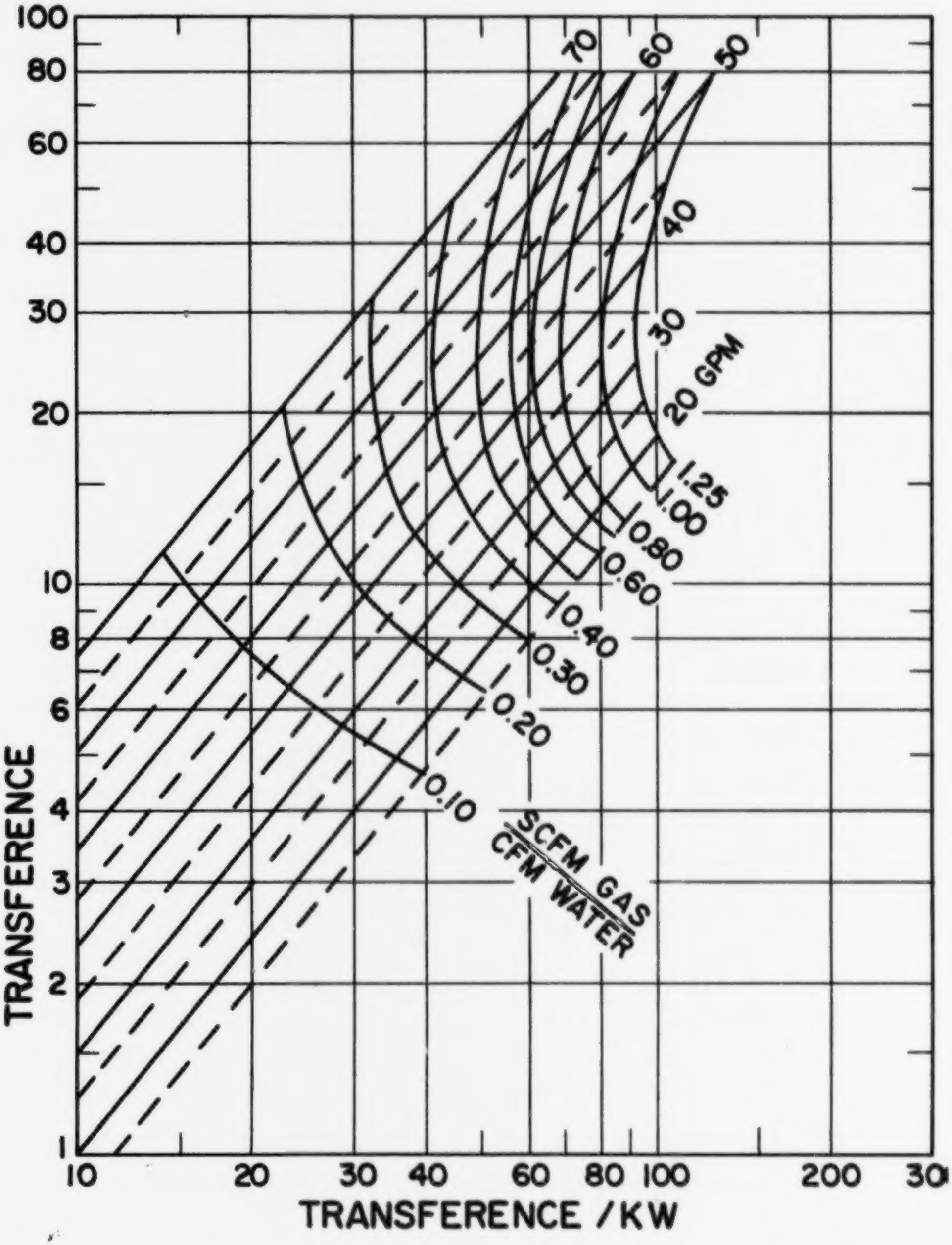

Figure 43. CORRELATION OF PILOT PLANT MIXER PERFORMANCE: T vs (T/KW) FOR VARIOUS GAS TO LIQUID VOLUME RATIOS AND WATER FLOW RATES

displacement-type level control which actuated the throttling valve on the discharge of the transfer pump at the bottom of the barometric leg.

Dryer

The recycle dryer used in the pilot plant consisted of two activated alumina beds through which the gas flow alternated about every 10 minutes. While one bed was on stream, the other was being regenerated by the pressure-swing technique.

The water saturated recycle gas was first compressed to about 55 psig and cooled to ambient temperature whereupon about three-quarters of the moisture condensed and was physically separated. The compressed gas then flowed through the adsorbent bed for further drying to a dew point of less than -60°F. A portion, about one-quarter, of the dry compressed gas was expanded to low pressure and used to purge the off-stream adsorbent bed for regeneration. The purge gas was ultimately returned to the compressor inlet. The remainder of the dry compressed gas was expanded through a pressure regulating valve and fed to the ozone generator.

Pressure-swing adsorbent dryers are compact, inexpensive, and simple and safe to operate. Thus, they are very well suited for pilot scale operations. However, because of the high gas pressures required, their operating costs are comparatively high.

For large installations, it has generally been found more economical to use a refrigerated predryer to reduce the gas dew point to about 35°F by condensation followed by a heat regenerated adsorption dryer. Such units are available in many sizes from several different manufacturers.

SECTION IX

ECONOMIC ANALYSIS OF LARGE PLANTS FOR OZONE TREATMENT OF WASTEWATER

Introduction

Economic analysis is necessarily an iterative process. Equipment sizes and process parameters must be specified before cost estimates can be made, and the cost estimates must be available before equipment sizes and process parameters can be optimumly specified. The approach taken here is to make initial cost estimates on the basis of reasonable estimates of equipment sizes and process parameters and later to linearly perturb these estimates to arrive at more nearly optimum sizes and parameters.

Because the ozone dosage required for a constant quality product water increases rapidly with increasing feedwater COD (see Fig 25), ozone wastewater treatment appears to be best suited for final, tertiary treatment. In the regime of tertiary treatment, the capital and operating costs of large ozone treatment plants will depend primarily on the COD of the plant feedwater and the hydraulic load.

The feedwater for a large ozone treatment plant may come directly from a secondary treatment process, or it may have received varying degrees of tertiary pretreatment. Thus, the feedwater COD might range from about 20 to 60 mg/l.

The required ozone dosage will vary with the specified feed and product COD values. For initial cost estimating purposes, however, the use of ozone dosage as an independent

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design parameter is somewhat inconvenient in that it requires assumptions about mixer efficiencies. A more convenient parameter is the ozone feed ratio, F*, which is defined as the total milligrams of ozone generated per liter of water treated (numerically equal to pounds ozone generated per million pounds of water treated).

In order to examine the economic effects of varying ozone requirements, plant cost estimates were prepared for three different ozone feed ratios: 40, 75, and 100 mg/l. And to examine the effects of plant scale, estimates for plants of 1, 10, and 50 million gallons per day (Mgd) nominal capacity were prepared for each ozone feed ratio. (Since the overall oxygen consumption partly depends on the actual COD reduction, for this purpose, COD reductions of 10, 20, and 25 mg/l were assumed for the ozone feed ratios of 40, 75, and 100 mg/l, respectively.)

The cost estimates for large plants are based on a direct scale-up of the pilot plant equipment with only two minor changes. First, a combination of a refrigerated predryer and a heat-regenerated adsorption dryer was selected instead of the pressure-swing adsorption dryer. And second, three instead of six reactors are used. Each of the reactors has a 15 minute detention time for a total treatment time of 45 minutes, and the product holding tank has a detention time of 15 minutes.

The cost estimates for all of the projected plants are based on the following assumptions.

1. The plant will operate continuously at designed load.
2. At least two parallel trains of equipment are required for process reliability.

3. All mechanical and electrical equipment is to be inside buildings.
4. A 20% excess ozone generating capacity will be installed.
5. Utility connections are available at site.
6. No feedwater pH adjustment is required.
7. Land costs are not included.
8. No service or administrative buildings are included.

The basic design parameters used for initial estimating purposes are summarized in Table 11. These cost estimates are generally comparable with published estimates for other tertiary treatment processes. However, these estimates are intended to be conservative. For example, the capital costs of major equipment were, where possible, taken as the average of two or more quoted costs instead of the lowest quoted cost.

One Mgd Plant

A schematic diagram of a one million gallon per day plant is illustrated in Fig 44. Two trains (only one is shown) of four, above-ground, bitumastic lined, cylindrical steel tanks are employed. The first three tanks in each train are reactors, and the fourth is the product holding tank. Each tank is 8 ft diameter. The first tank in each train is 25 ft high, and the remainder are 20 ft high. The additional height of the first reactor is for handling possible surfactant foam.

The process arrangement is essentially that used in the pilot plant. In order to accommodate variations of feedwater flow rate, water recycle around the first reactor is automatically controlled by a float valve in the sump

TABLE 11

DESIGN PARAMETERS FOR INITIAL COST ESTIMATES FOR LARGE OZONE WASTEWATER TREATMENT PLANTS

Feedwater flow, 10^6 gal/day	1	10	50
Parallel trains of three, 15 min reactors	2	4	4
Ozone concentration, wt %	1.7	1.7	1.7
Ozone installed capacity, lb/day			
F* = 40 mg/l	400	4,000	20,000
F* = 75 mg/l	750	7,500	37,500
F* = 100 mg/l	1,000	10,000	50,000
Oxygen consumption, lb/day			
F* = 40 mg/l	450	4,500	22,500
F* = 75 mg/l	520	5,200	26,000
F* =100 mg/l	580	5,800	28,800
Electric power, Kw			
F* = 40 mg/l	150	1,500	7,600
F* = 75 mg/l	220	2,200	10,800
F* =100 mg/l	250	2,500	12,700
Gas flow, std ft^3/min			
F* = 40 mg/l	160	1,600	8,000
F* = 75 mg/l	310	3,100	15,500
F* =100 mg/l	410	4,100	20,500

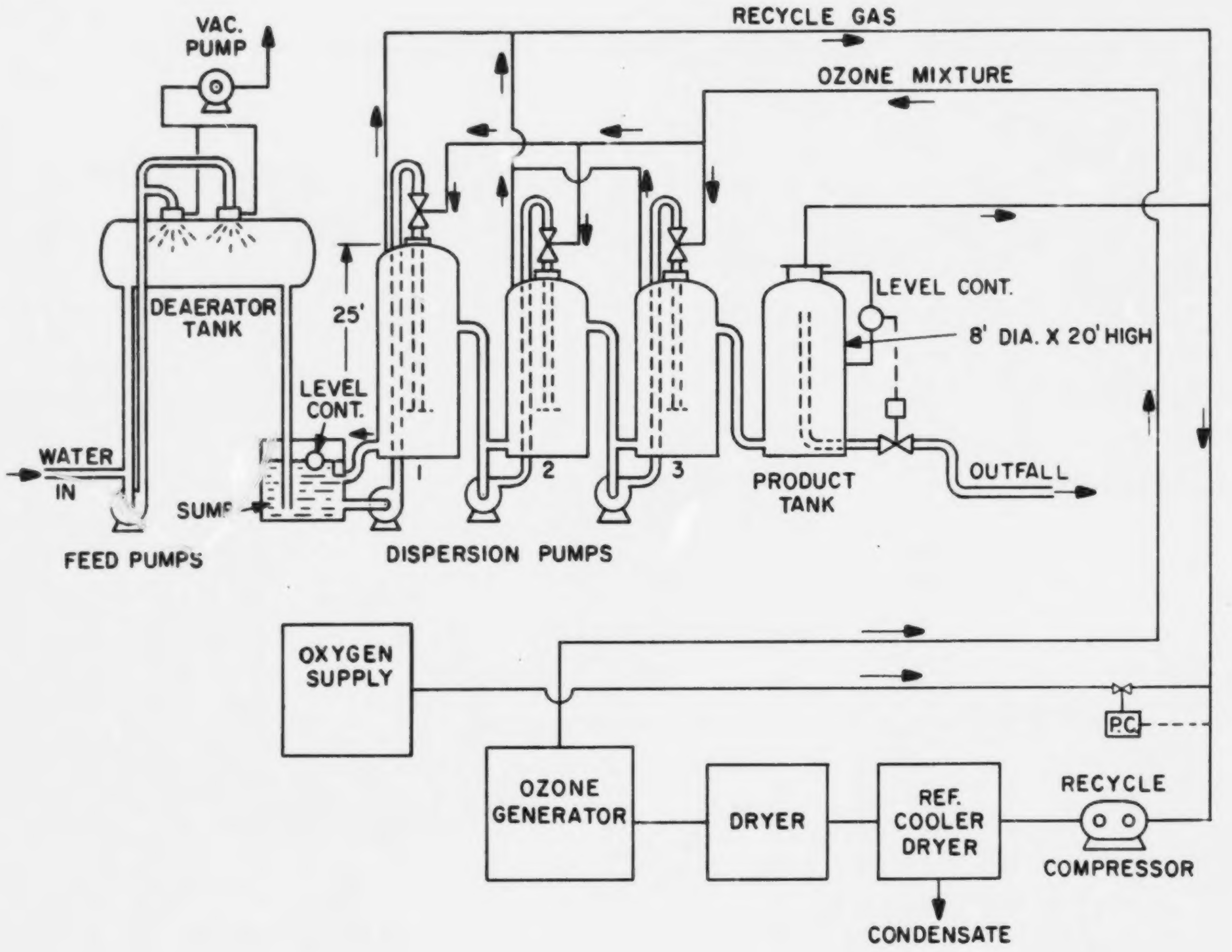
RECYCLE GAS
OZONE MIXTURE
VAC. PUMP
DEAERATOR TANK
25'
LEVEL CONT.
WATER IN
SUMP
FEED PUMPS
1
2
3
DISPERSION PUMPS
PRODUCT TANK
LEVEL CONT.
8' DIA. X 20' HIGH
OUTFALL
OXYGEN SUPPLY
P.C.
OZONE GENERATOR
DRYER
REF. COOLER DRYER
CONDENSATE
RECYCLE COMPRESSOR

Figure 44. FLOW DIAGRAM FOR 1 MGD WASTEWATER TREATMENT PLANT

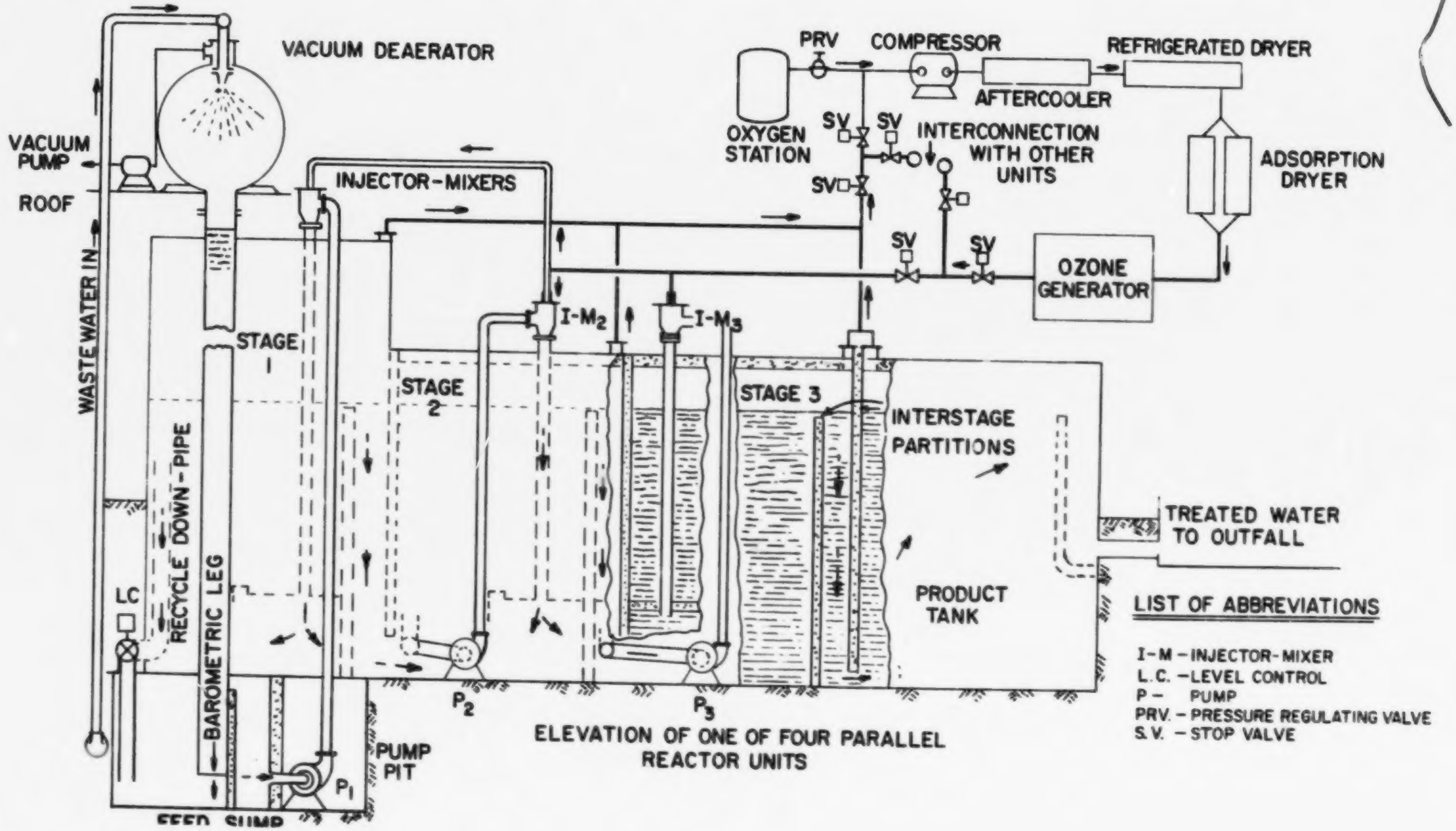
VACUUM DEAERATOR
VACUUM PUMP
ROOF
WASTEWATER IN
INJECTOR-MIXERS
STAGE 1
STAGE 2
STAGE 3
RECYCLE DOWN-PIPE
BAROMETRIC LEG
LC
FEED SUMP
PUMP PIT
P_1
P_2
P_3
$I-M_2$
$I-M_3$
OXYGEN STATION
PRV
COMPRESSOR
AFTERCOOLER
REFRIGERATED DRYER
ADSORPTION DRYER
SV
SV
SV
SV
SV
INTERCONNECTION WITH OTHER UNITS
OZONE GENERATOR
INTERSTAGE PARTITIONS
PRODUCT TANK
TREATED WATER TO OUTFALL
ELEVATION OF ONE OF FOUR PARALLEL REACTOR UNITS
LIST OF ABBREVIATIONS
I-M – INJECTOR-MIXER
L.C. – LEVEL CONTROL
P – PUMP
PRV. – PRESSURE REGULATING VALVE
S.V. – STOP VALVE

Figure 45. FLOW DIAGRAM OF 10 MGD WASTEWATER TREATMENT PLANT

feeding the first stage pump. The water recycle-bypass arrangement on the other reactors is the same used in the pilot plant which allows the mixer water flows to be varied independently of the feedwater flow.

10 and 50 Mgd Plants

Elevation and plan views of a projected 10 million gallon per day plant are shown in Fig 45 and 46. The process flow pattern and tank depths are the same as for the 1 Mgd plant. Four parallel trains of four, rectangular, reinforced concrete tanks are used: for larger plants, concrete tanks are less expensive than the bitumastic lined steel tanks. The concrete tanks form two walls of a building which houses the mechanical and electrical equipment on two floors. The lower floor contains the pumps, compressors and dryers, and the upper floor contains the ozone generators. The vacuum deaerators are mounted on the roof of the structure, and the vacuum pumps and ventilating fans are in an adjoining penthouse.

The layout of a 50 Mgd plant would be a direct scale-up of the 10 Mgd plant.

Costs of Major Equipment

The capital costs for the major items of process equipment are shown in Fig 47 through 52. These costs are based on vendors' quotations FOB factory during the fourth quarter of 1971. In several of the figures, the range of prices quoted by several manufacturers and the average of these prices are shown.

Costs of centrifugal pumps for driving the mixers are shown as a function of pump capacity in Fig 47. Ozone generator prices are shown in Fig 48 as a function of capacity when

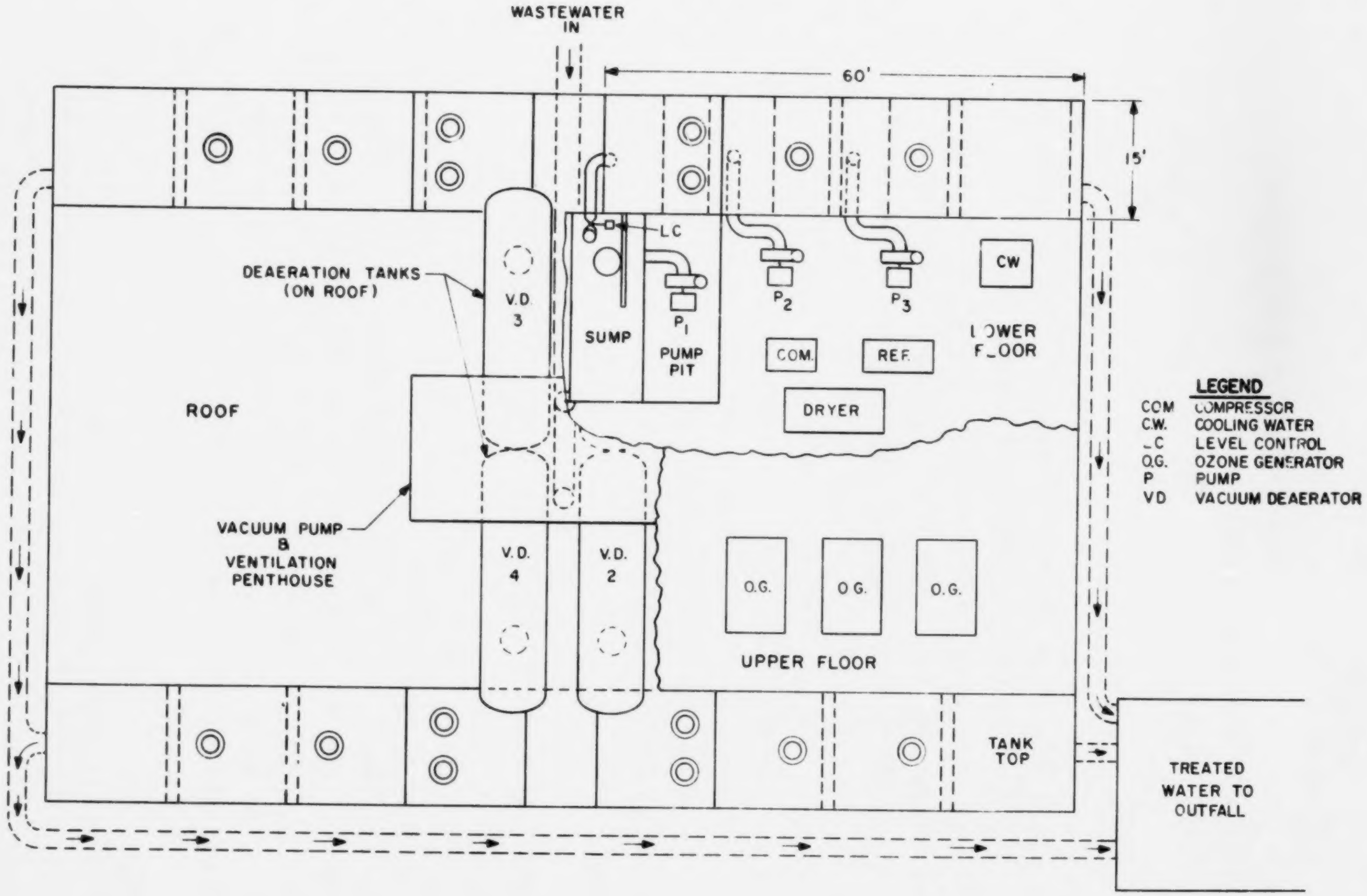
WASTEWATER IN
60'
15'
LC
DEAERATION TANKS (ON ROOF)
V.D. 3
SUMP
P1
PUMP PIT
P2
P3
CW
LOWER FLOOR
COM.
REF.
DRYER
ROOF
VACUUM PUMP & VENTILATION PENTHOUSE
V.D. 4
V.D. 2
O.G.
O.G.
O.G.
UPPER FLOOR
TANK TOP
TREATED WATER TO OUTFALL
LEGEND
COM COMPRESSOR
C.W. COOLING WATER
LC LEVEL CONTROL
O.G. OZONE GENERATOR
P PUMP
VD VACUUM DEAERATOR

Figure 46. MULTILEVEL PLAN VIEW OF 10 MGD WASTEWATER TREATMENT PLANT

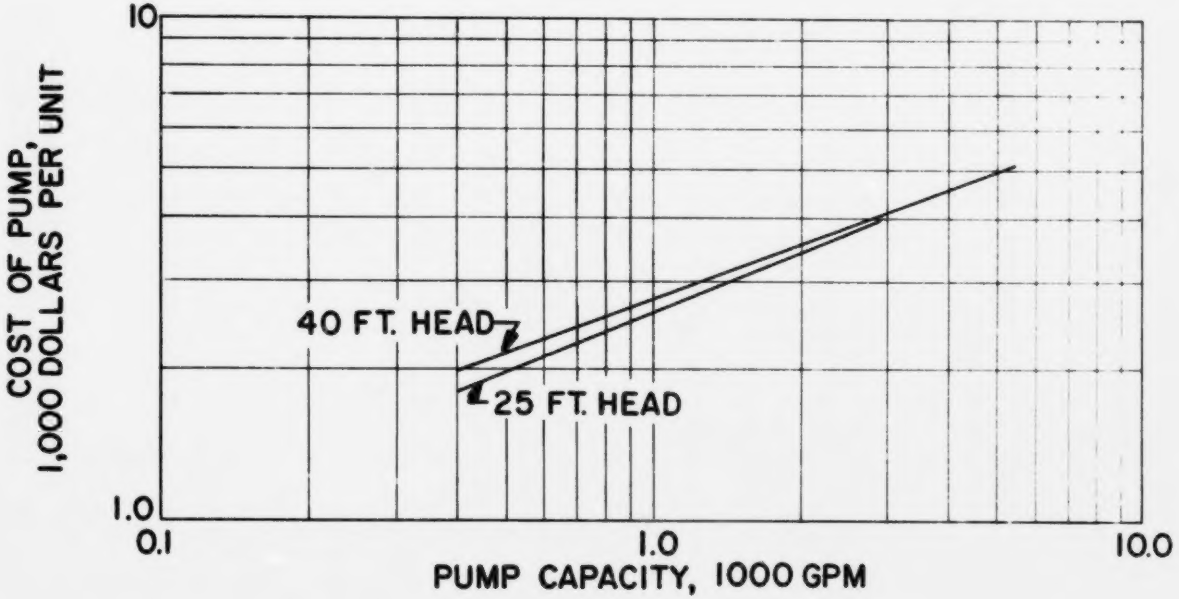

Figure 47. CENTRIFUGAL PUMP CAPITAL COSTS

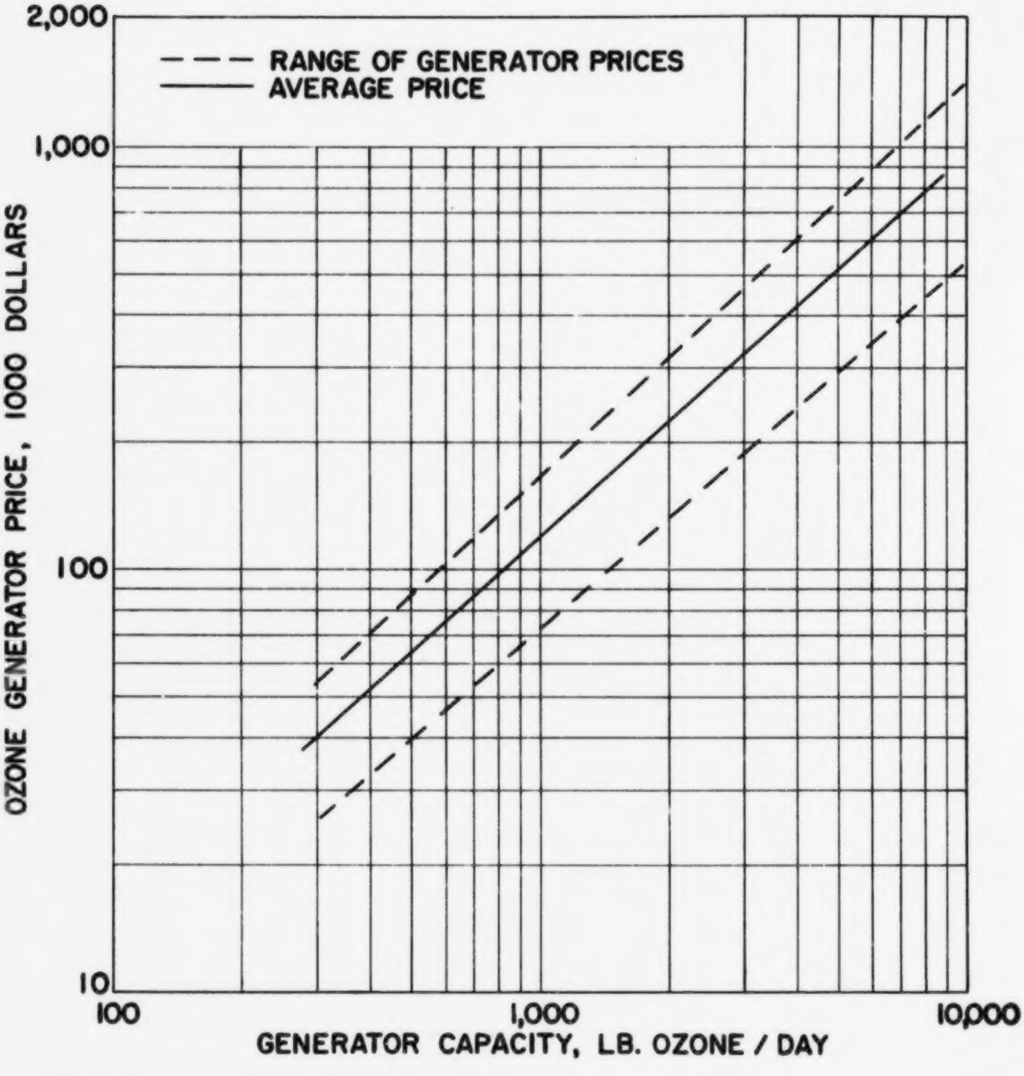

Figure 48. OZONE GENERATOR CAPITAL COSTS

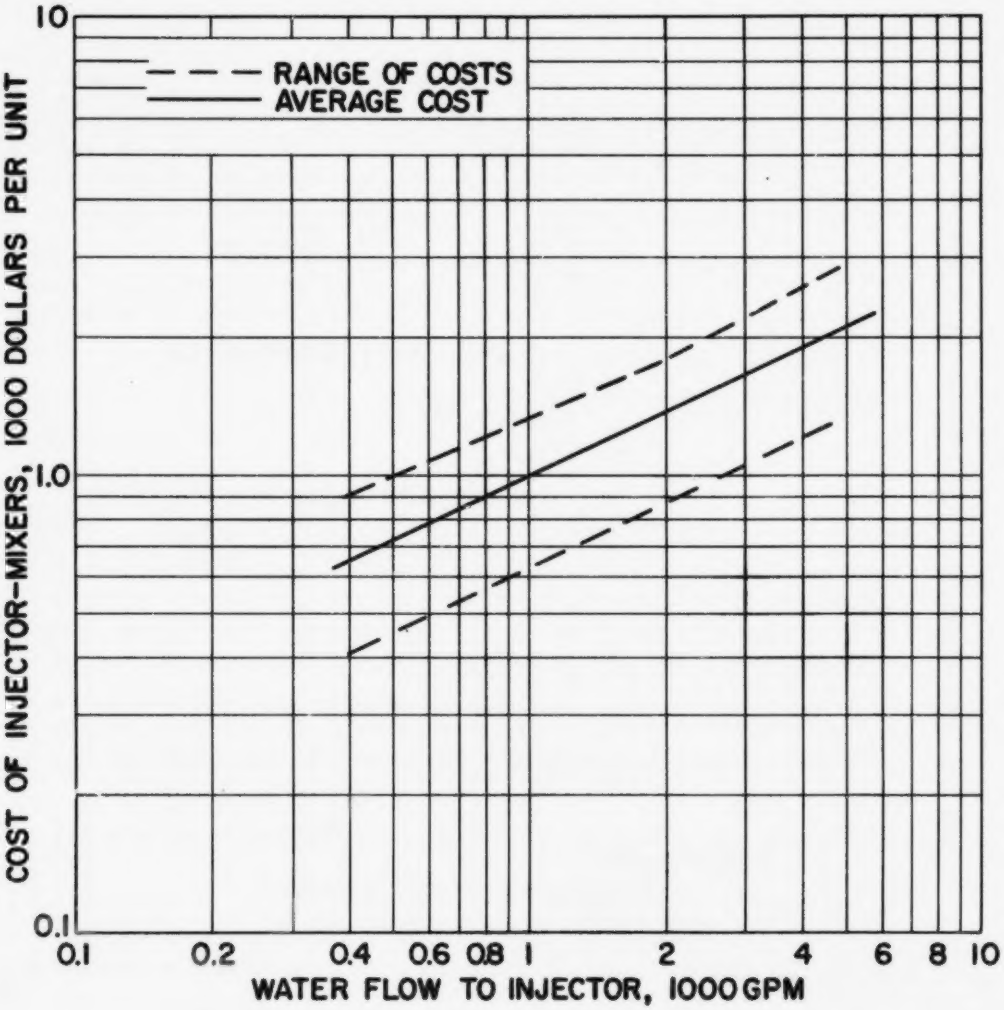

Figure 49. INJECTOR-MIXER CAPITAL COSTS

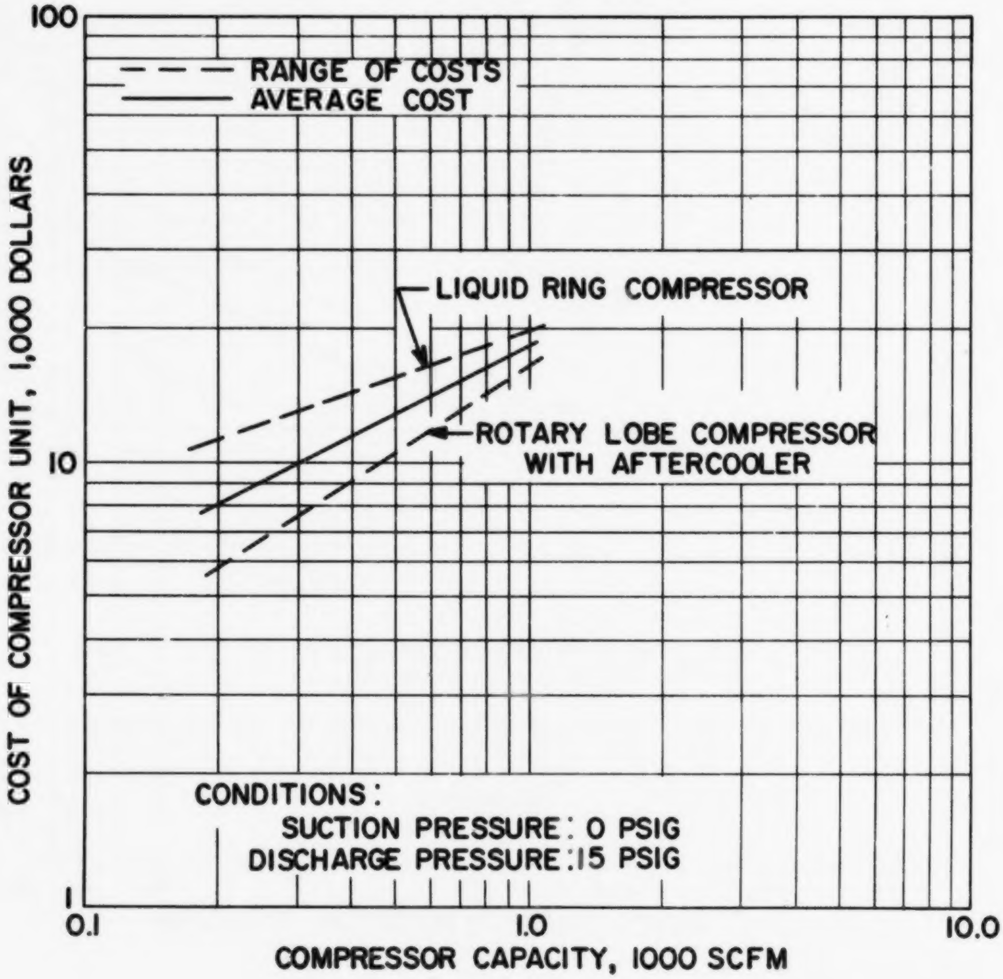

Figure 50. OXYGEN COMPRESSOR CAPITAL COSTS

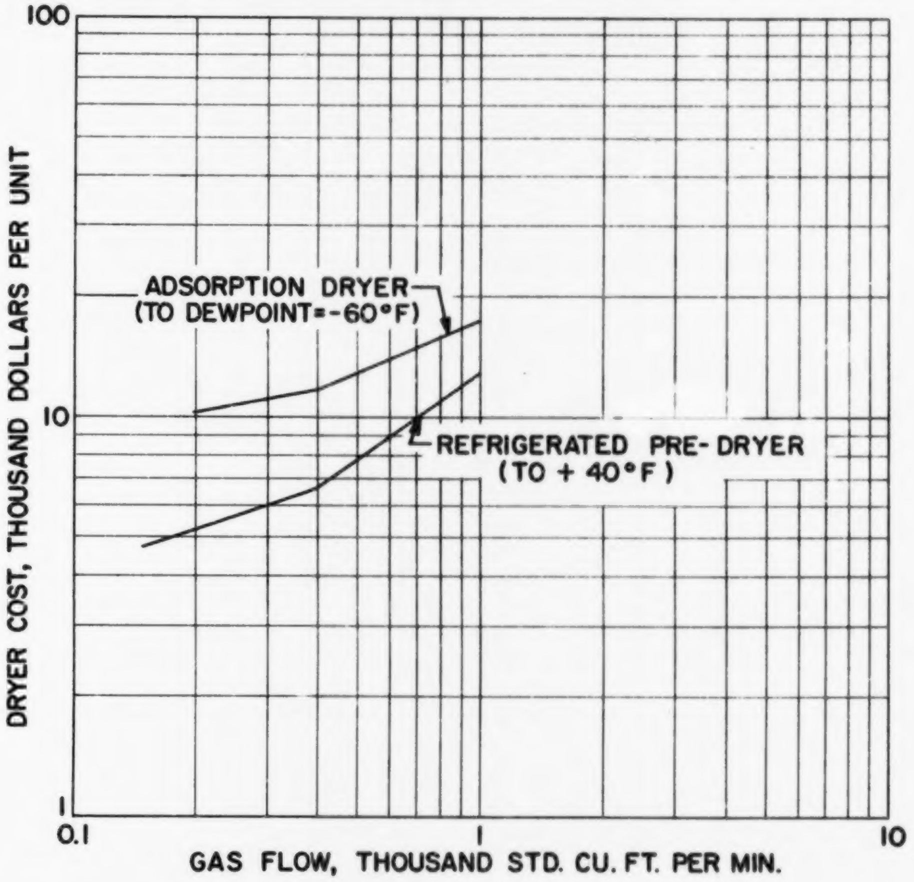

Figure 51. GAS DRYER CAPITAL COSTS

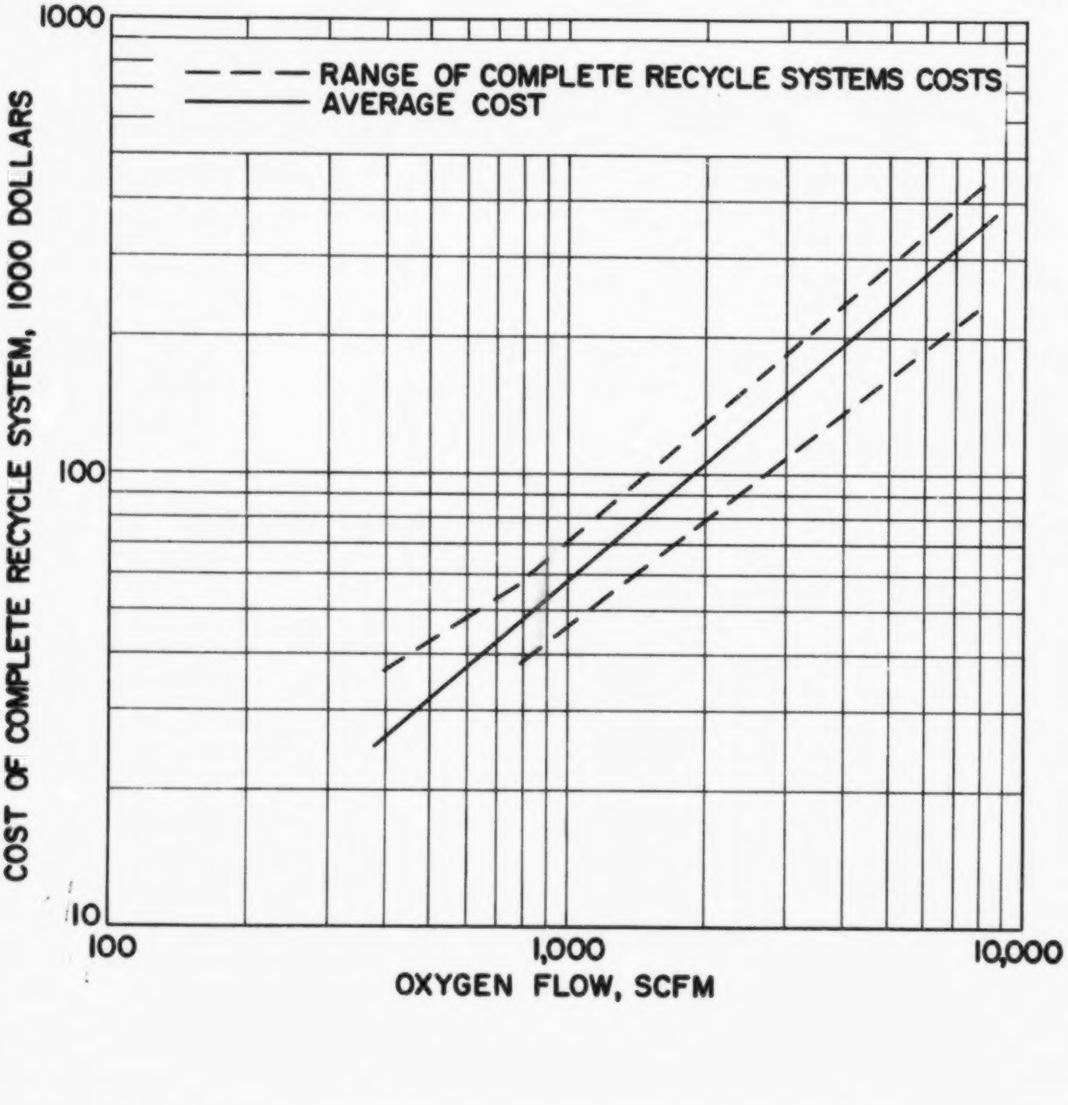

Figure 52. CAPITAL COSTS OF INTEGRATED OXYGEN RECYCLE SYSTEMS

generating 1.7 wt percent ozone in oxygen. The costs of injector mixers are shown as a function of nominal water flow rate in Fig 49. Prices for two types of oxygen compressors, liquid ring compressors as used in the pilot plant and rotary lobe compressors with aftercooler, are shown as a function of capacity in Fig 50. Capital costs for refrigerated predryers and heat-regenerated adsorption dryers are shown in Fig 51. Capital costs for integrated gas recycle systems - - compressors and dryers - - are shown in Fig 52.

Capital Cost Estimates

The capital cost estimates for nine combinations of plant sizes and ozone feed ratios are summarized in Table 12. Costs for the major items of process equipment were taken from the average curves in Fig 47 through 51, and allowance was made for shipping and erecting. Costs of foundations, buildings, piping, instruments, and electrical work were estimated from approximate plant layouts and pipe drawings using either vendors' quotations or published estimating tables (16-19). Engineering, contractor's overhead, and fees were taken as 30% of direct materials and labor.

The estimated costs reflect average construction costs for the fourth quarter of 1971. These estimates are intended to be conservative, but costs at specific locations may easily vary ± 35% from such general estimates.

Operating Costs

Estimates of the operating costs for the nine combinations of plant sizes and ozone feed ratios are summarized in Table 13 and are shown graphically in Fig 54. A percentage break-down of estimated operating costs is shown in Table 14. A graphical break-down of the operating costs of large plants

Table 12

CAPITAL COST ESTIMATES FOR PLANTS TO TREAT WASTEWATER WITH OZONE

Plant Capacity, mgd	1	10	50
Ozone Feed Ratio, lb $O_3/10^6$ lb H_2O	40	40	40
Item	Capital Costs, 1000 Dollars		
Deaerators	8	51	160
Process pumps	20	67	390
Injector mixers	7	31	140
Reactors & Holding tanks	70	200	450
Oxygen compressors	8	48	230
Dryers	11	64	310
Ozone generators	53	440	1,980
Sumps & Drains	10	35	85
Ozone decomposer	1	6	15
Piping	34	110	480
Electrical	20	120	530
Instrumentation	21	44	80
Painting	5	10	40
Site work	10	20	60
Equipment supports & building	50	140	800
Total Materials & Labor	328	1,386	5,750
Engineering, Contractor's overhead and fee	98	416	1,725
Total Capital Cost	426	1,802	7,475

Table 12 continued

CAPITAL COST ESTIMATES FOR PLANTS TO TREAT WASTEWATER WITH OZONE

Plant Capacity, mgd	1	10	50
Ozone Feed Ratio, lb $O_3/10^6$ lb H_2O	75	75	75
Item	Capital Costs, 1000 Dollars		
Deaerators	8	51	160
Process pumps	20	67	390
Injector mixers	7	31	140
Reactors & Holding tanks	70	200	450
Oxygen compressors	10	76	280
Dryers	13	104	390
Ozone generators	94	770	3,465
Sumps & Drains	10	35	85
Ozone decomposer	1	6	15
Piping	34	136	520
Electrical	24	140	550
Instrumentation	21	44	80
Painting	6	10	40
Site work	10	20	60
Equipment supports & building	50	150	800
Total Materials & Labor	378	1,840	7,425
Engineering, Contractor's overhead and fee	113	552	2,227
Total Capital Cost	491	2,392	9,652

Table 12 continued
CAPITAL COST ESTIMATES FOR PLANTS TO TREAT WASTEWATER WITH OZONE

Plant Capacity, mgd	1	10	50
Ozone Feed Ratio, lb $O_3/10^6$ lb H_2O	100	100	100
Item	Capital Costs, 1000 Dollars		
Deaerators	8	51	160
Process pumps	20	67	390
Injector mixers	7	31	140
Reactors & Holding Tanks	70	200	450
Oxygen compressors	12	90	380
Dryers	15	122	490
Ozone generators	122	980	4,410
Sumps & Drains	10	35	85
Ozone decomposer	1	6	15
Piping	34	136	520
Electrical	26	153	600
Instrumentation	21	44	80
Painting	6	10	40
Site work	10	20	60
Equipment supports & building	50	150	800
Total Materials & Labor	412	2,095	8,620
Engineering, Contractor's Overhead and fee	124	628	2,586
Total Capital Cost	536	2,723	11,206

with an ozone feed ratio of 100 mg/l is shown in fig 55.

The operating cost estimates are based on continuous operation at designed capacity. Electrical power costs were assumed to be 1.4, 1.1, and 0.9 ¢/Kwh for the 1, 10, and 50 Mgd plants, respectively. Oxygen costs are based on typical merchant liquid oxygen prices (including customer station rental) which are shown as a function of usage rate in Fig 53.

Plant amortization is based on 25 years life and 5% annual interest which corresponds to an annual amortization charge of 7.1 percent of capital cost. Maintenance costs were taken as one percent of capital costs per year. Incremental operating labor was assumed to be 4 man-hours/day for the 1 Mgd plant and 8 man-hours/day for the 10 and 50 Mgd plants at $5.00 per man-hour plus 30% for overhead and supervision.

Cost Optimization

All of the preceding cost estimates are based on an initial set of reasonable, but assumed plant parameters. Now, in order to arrive at more nearly optimal plant parameters, a procedure for linearly perturbing the initial estimates to minimize the projected operating costs will be described and illustrated.

Once the requirements for a specific ozone wastewater treatment plant are established, a number of plant parameters should be concurrently adjusted to yield a minimum total treatment cost. Many such parameters can be optimized only for specific situations and specific plant locations. However, three plant parameters can be optimized for more general cases: the concencentration of ozone generated (c_g), the mixer sizes and flow rates, and the distribution of

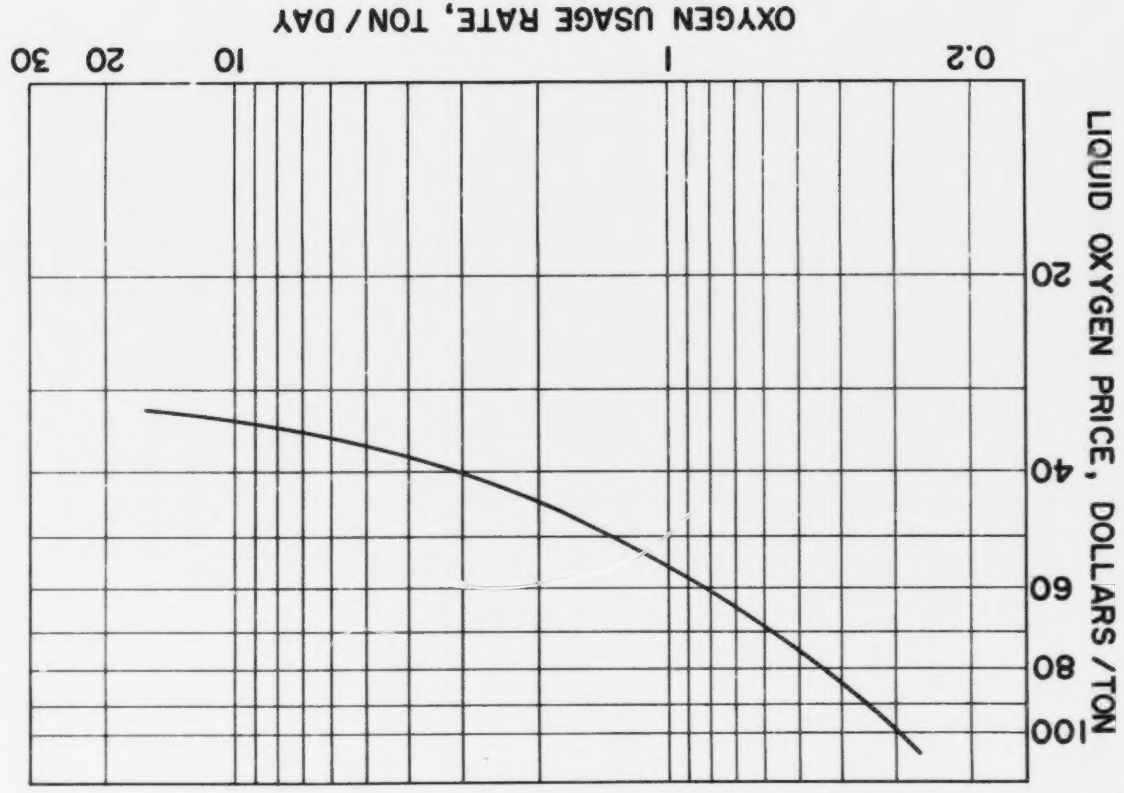

Figure 53. TYPICAL COSTS OF MERCHANT LIQUID OXYGEN AS A FUNCTION OF USAGE RATE

TABLE 13

ESTIMATED ANNUAL OPERATING COSTS OF OZONE WASTEWATER TREATMENT PLANTS IN THOUSAND DOLLARS

1 MILLION GAL/DAY PLANT F*, mg/l =	40	75	100
Electric power	19	26	31
Amortization	30	35	38
Oxygen	9	11	12
Operation & Maintenance	15	16	16
Total	73	88	97
¢/1000 gal	20.0	24.1	26.6

10 MILLION GAL/DAY PLANT F*, mg/l =	40	75	100
Electric power	147	208	245
Amortization	128	170	193
Oxygen	37	44	48
Operation & Maintenance	41	47	50
Total	353	469	536
¢/1000 gal	9.7	12.8	14.7

50 MILLION GAL/DAY PLANT F*, mg/l	40	75	100
Electric power	600	855	1002
Amortization	531	685	796
Oxygen	135	159	174
Operation & Maintenance	99	120	136
Total	1365	1819	2108
¢/1000 gal	7.5	10.0	11.6

TABLE 14

PERCENTAGE BREAKDOWN OF ESTIMATED ANNUAL OPERATING COSTS OF OZONE WASTEWATER TREATMENT PLANTS

1 MILLION GAL/DAY PLANT F*, mg/l =	40	75	100
Electric power	26.0	29.5	31.9%
Amortization	41.2	39.8	39.2
Oxygen	12.3	12.5	12.4
Operation & Maintenance	20.5	18.2	16.5

10 MILLION GAL/DAY PLANT *F, mg/l =	40	75	100
Electric power	41.6	44.4	45.7%
Amortization	36.3	36.2	36.0
Oxygen	10.5	9.4	9.0
Operation & Maintenance	11.6	10.0	9.3

50 MILLION GAL/DAY PLANT F*, mg/l =	40	75	100
Electric power	44.0	47.0	47.5%
Amortization	38.9	37.7	37.8
Oxygen	9.9	8.7	8.2
Operation & Maintenance	7.2	6.6	6.5

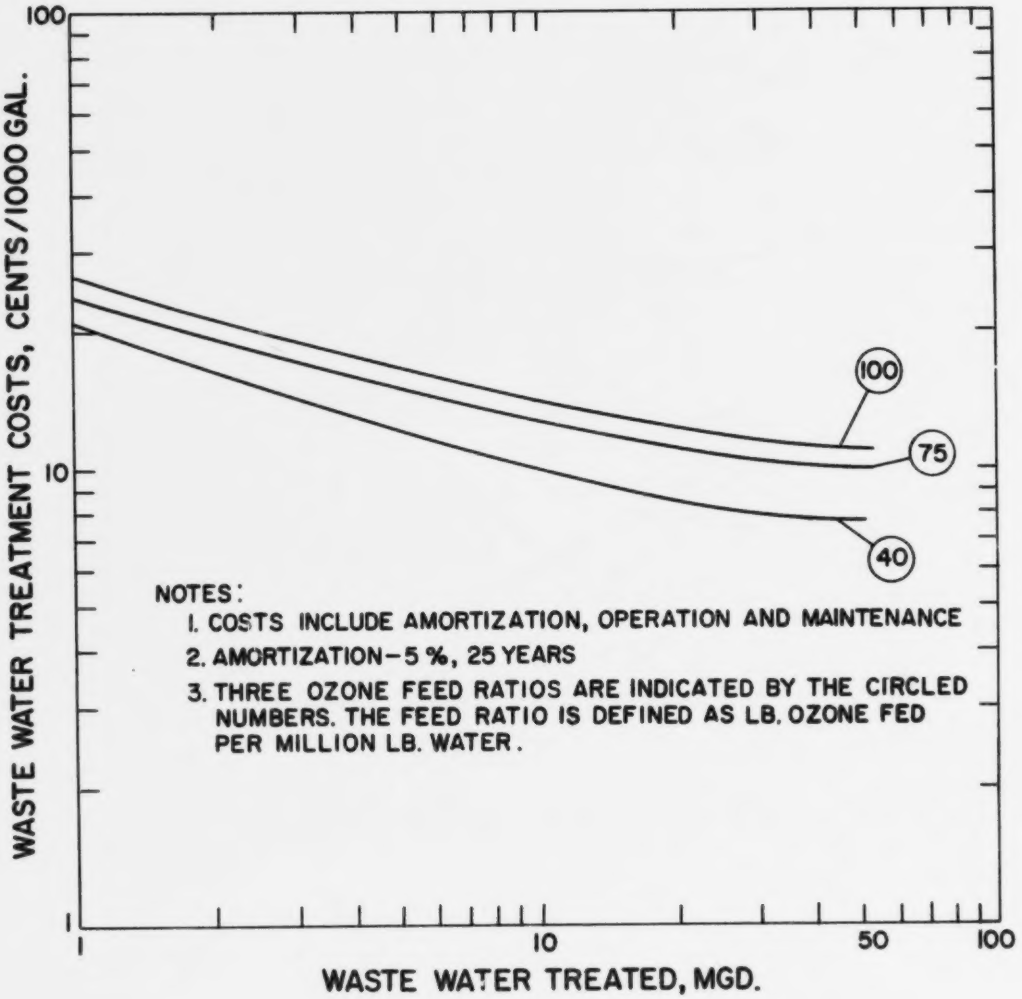

Figure 54. TOTAL OPERATING COSTS FOR OZONE TREATMENT OF WASTEWATER AT DIFFERENT OZONE FEED RATIOS

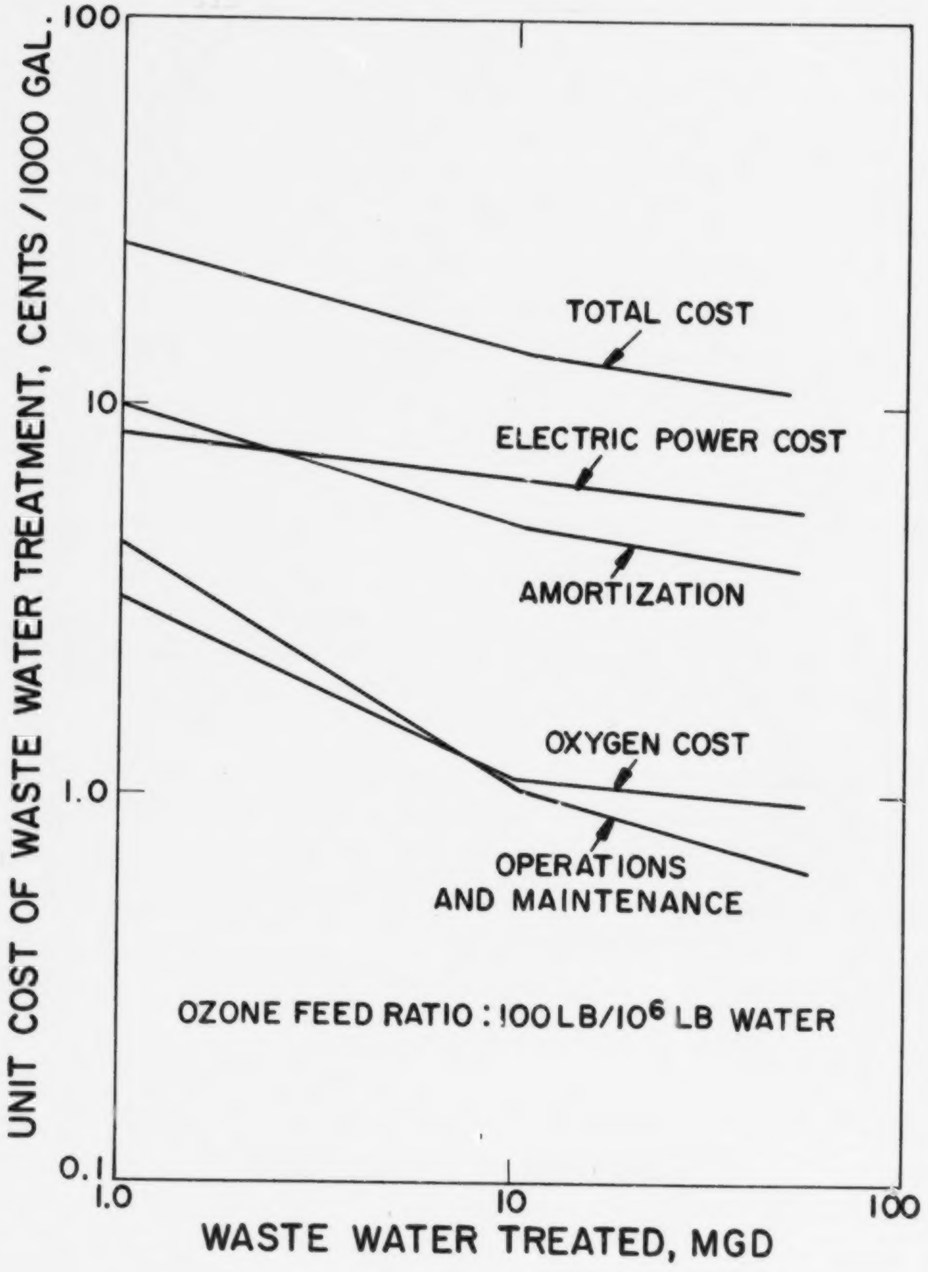

Figure 55. BREAKDOWN OF UNIT COST FOR TREATING WASTEWATER WITH OZONE

dissolved ozone concentrations (Z_i) along the train of reactors.

As was illustrated in the discussion of the COD correlations, once the COD and flow requirements of an ozone wastewater treatment plant are specified, the quantity of ozone to be dissolved can be calculated. With the additional specification of treatment time and feedwater pH, the time weighted average dissolved ozone concentration (Z^*) can be calculated. For cost optimization, one further requires estimates for ozone production costs as a function of c_g, correlations for the performance of the mixers, and some simple method for characterizing the Z_i distribution. (Note that establishing the value of Z^* does not uniquely define the Z_i distribution.)

Ozone Production Costs. Ozone production costs depend on the concentration generated, scale of production, power rates, and the specific type of generators used. The costs associated with producing a pound of gaseous ozone are taken to be all those power and capital amortization costs required to deliver a pound of gaseous ozone in oxygen to the gas-liquid mixers at 11 psig, assuming recycle oxygen at 2 psig and a 4 psi pressure drop in the gas system. Specifically included are the amortization and power requirements for the gas compressors, gas dryers, and ozone generators.

The scale of production will be assumed to be that of the 10 mgd plant with an ozone feed ratio of 75 lb/million lb water, described in the initial cost estimates, which has an installed ozone generating capacity of 7500 lb/day. Linear scaling rules will be used for adjusting amortization and power costs from this base. Power rate is taken as 1.1¢/Kwh and amortization charge as 7.1% of capital investment/year.

Ozone generation costs are taken from two sources: equipment price quotations for units generating 1.7 wt % ozone in oxygen, and the operating characteristics of the pilot plant ozone generator. Power requirements were taken from Figure 36 (the 20 scfm curve), and equipment capacity as a function of c_g was calculated from the same data assuming a maximum 10 Kw input to the pilot plant generator. Gas compression and drying costs were taken from price quotations and manufacturers' equipment specifications.

The resulting estimated costs for producing a pound of gaseous ozone are shown as a function of c_g in Figure 56. For mathematical purposes of optimization, precise and smooth production costs are required. Therefore, the total production cost curve is shown on expanded scale in Figure 57.

As the ozone concentration increases, the costs for generator power and amortization increase. But because higher concentrations decrease the volume of gas to be handled, the costs of compressing and drying decrease with increasing concentration. These opposing trends combine to yield a shallow minimum in the total production cost at about 1.7 wt % ozone.

The magnitude of the various components of ozone production costs is noteworthy. The major part is associated with the ozone generators. The largest fraction is ozone generator power costs, and the next largest is generator amortization. Costs for compressing and drying the recycle gas vary from 20% of the total cost at 2 wt % ozone to 6% at 4 wt % ozone.

The statement is often made that producing ozone from pure oxygen is less expensive, even including the cost of oxygen, than is production from air. The total production costs shown here offer a basis for quantifying that statement. Generally, an ozone generator operating at constant power will produce about half the concentration of ozone operating on air that it will produce operating on oxygen. Thus, the production of a pound of ozone from air will consume twice the power and require twice as large generators as would be required for production from oxygen. The volume of gas to be compressed and dried would also be doubled using air. Thus the cost of producing a pound of ozone at 1% concentration in air would be about 16¢ compared to 8¢/lb at 2% ozone using oxygen. Comparison of production costs at the same ozone concentrations are even more favorable for oxygen.

The substantial savings in ozone production costs are partly offset by the additional cost of oxygen. In ozone wastewater treatment, oxygen is consumed both by COD reduction, which is proportional to ozone dosage, and by the increase of dissolved oxygen (DO) concentration, which is proportional only to the quantity of water treated. For the 10 Mgd plant with F* of 75 mg/l, the oxygen costs are about 1.6¢/lb ozone produced, about 1/3 being attributable to COD reduction and 2/3 to increasing the DO concentration. Thus in this case, the additional oxygen cost is small compared with the savings in production costs.

For very small ozone doses, however, most of the oxygen consumption would be from increasing the DO concentration, and the oxygen cost per pound of ozone produced might be greater than the savings in ozone production costs. It must be emphasized that the additional oxygen costs would not be without benefit; for the high DO content in the product water is generally very desirable. And of course, it is technically feasible to recover a major part of the DO by vacuum deaeration after ozone treatment.

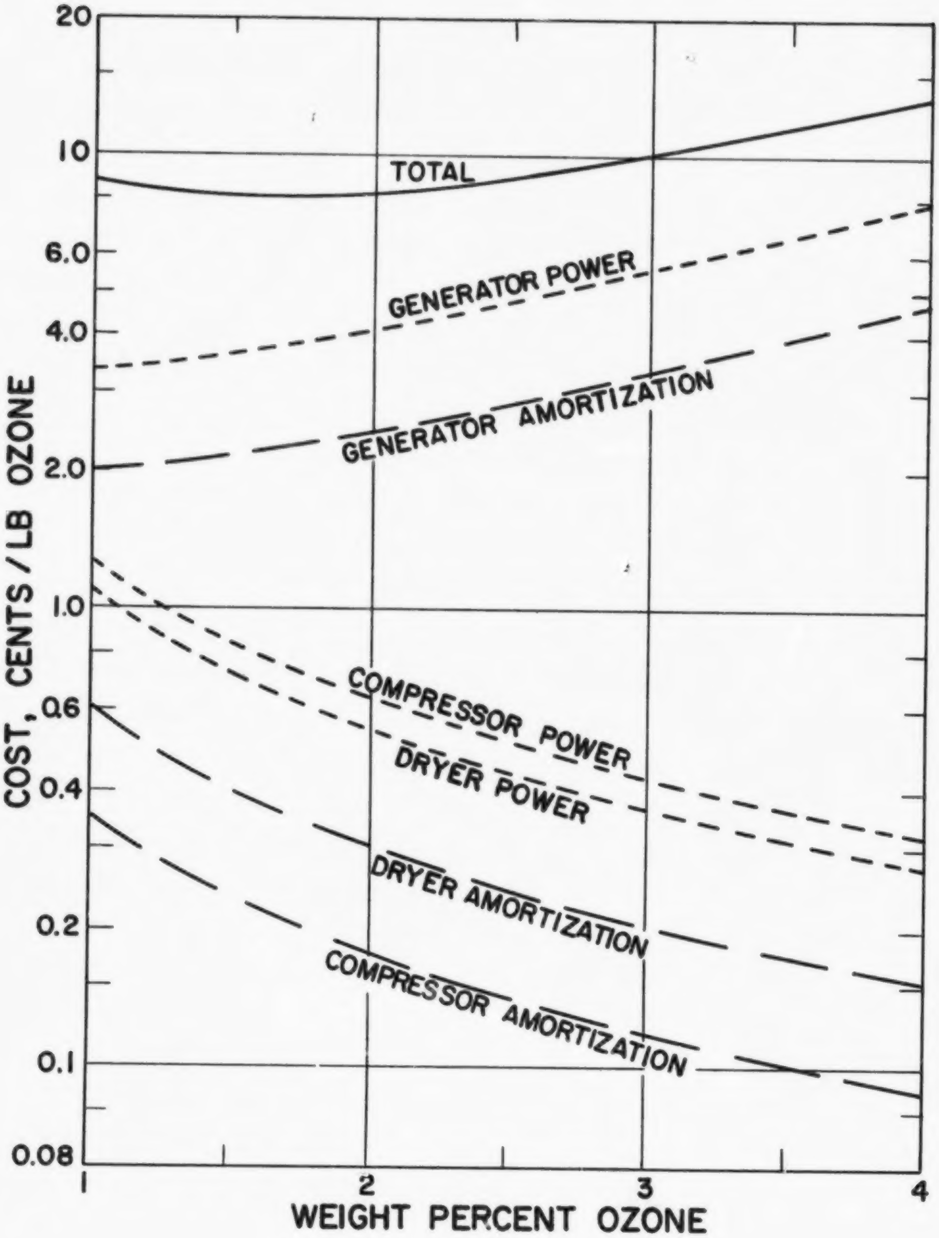

Figure 56. ESTIMATED TOTAL PRODUCTION COST OF OZONE IN A TYPICAL WASTEWATER TREATMENT PLANT

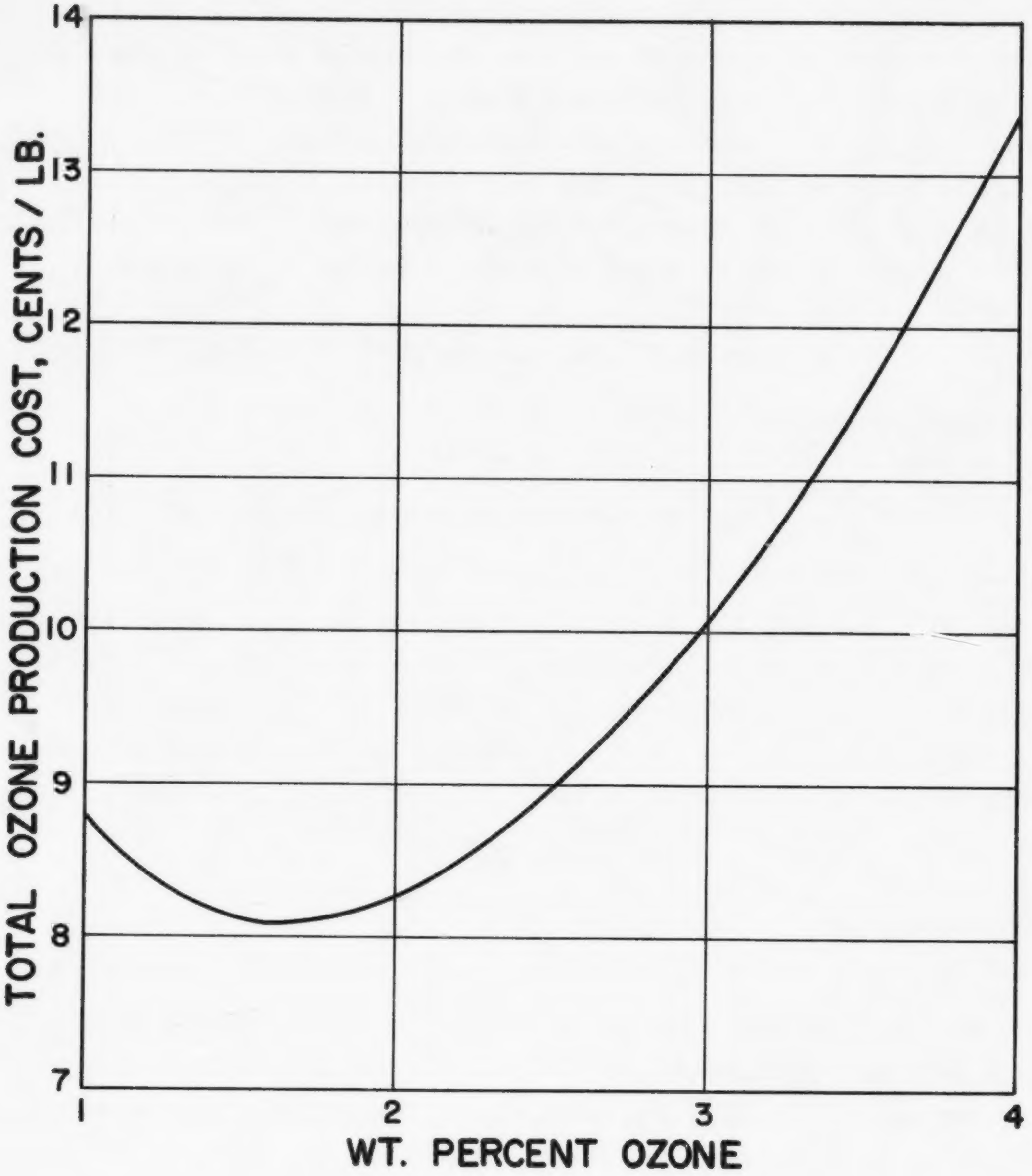

Figure 57. EXPANDED GRAPH OF ESTIMATED TOTAL PRODUCTION COST OF OZONE

Optimizing Mixer Sizes

Optimizing the size and operating parameters of the gas-liquid mixers is based on scaling the mixers used in the pilot plant. In this section, primed (') symbols will be used for the full scale plant variables and not-primed symbols will signify a pilot plant variable. Since the pilot plant mixers were found to operate most effectively at 55 gpm water flow, a plant scaling factor X'_p will be defined on that flow basis.

$$X'_p \equiv \text{(designed plant feed, gpm)/(55 gpm)} \qquad (26)$$

In order to allow adjustment of (G/L) for each mixer, a mixer scaling factor X'_m must be defined.

$$X'_m \equiv \text{(flow through mixer)/(plant feed flow)} \qquad (27)$$

X'_m is also the recycle ratio for a mixer. If X'_m is greater than one, part of the mixer flow is recycle from the bottom of the reactor. If X'_m is less than one, part of the feed is by-passed to the bottom of the reactor. In the pilot plant, X'_m values from 0.54 to 2.75 at mixer flows of 20 and 35 gpm were used. There was no evident effect of X'_m on transference, and there would presumably be none at 55 gpm.

The basic mixer scaling rule is as follows.

$$T' = X'_p X'_m T \qquad (28)$$

For the i-th stage, the value of D_i (lb O_3 dissolved in the i-th stage/lb COD feed) can be calculated as shown in the discussion of the COD correlations. The actual pounds of ozone to be dissolved per hour, Q'_i, is as follows.

$$Q' = 0.02749\ D_i L_f X'_p \qquad (29)$$

From the definition of $T' = Q'/\Delta p_m$, the required average partial pressure driving force, Δp_m, is as follows.

$$\Delta p_m = 0.02749\ D_i L_f / X'_m T \qquad (30)$$

Using Eq (30) and the base mixer flow, the gas to liquid volume ratio is as follows:

$$(G/L) = 0.07526\ D_i L_f / X'_m c_g f \qquad (31)$$

where c_g is the wt % ozone in gas

f is the fraction of feed ozone dissolved.

Solving Eq (30) and (31) for $X'_m/D_i L_f$ and equating the results, the following equation is obtained in which it is noted that Δp_m is a function of c_g, f and Z. [See Eq (22)]

$$c_g f/\Delta p_m(c_g, f, Z) = 2.7376\ T/(G/L) \qquad (32)$$

Notice that all scaling factors have disappeared from Eq (32). A simple function of c_g, f, and Z is proportional to the ratio of transference to G/L for any size mixer in any size plant.

A numerical inspection of $c_g f/\Delta p_m$ shows it to increase when f increases. Since maximum values for f are desired, it follows that the maximum value of T/(G/L) is desired. An inspection of the mixer performance correlation, Figure 43, shows this maximum for the pilot plant mixers to be at 55 gpm and G/L = 1 where T = 80. Substituting the latter two values into Eq (32) the following is obtained.

$$c_g f/\Delta p_m(c_g, f, Z) = 219 \qquad (33)$$

Equation (33) offers a basis for optimizing the mixers. For specific values of c_g and Z, Eq (33) can be solved for f, the fraction of feed ozone that can be dissolved by mixers of the type used in the pilot plant operating at optimum conditions. Having f, the value of X'_m can be calculated directly from Eq (31) using (G/L) = 1.

Unfortunately, there is no analytic solution for Eq (33). It is transcendental in f and c_g and therefore requires an iterative solution. For convenience, values of f for various values of c_g and Z are given in Table 15 for a typical situation in which $P_2 = 2$ psig, $d = 0.21$, and $H = 541$ mg/l/atm. From this table, it is evident that the fraction ozone dissolved increases with increasing c_g and decreasing Z, exactly as a cocurrent mixer should behave.

The appropriate mixer power is simply that for liquid pumping; the compression work for the gas has been included in the ozone production cost. At 55 gpm and G/L = 1, the pilot plant mixers exhibited a 17-1/2 psi water pressure drop (and a gas pressure drop of 9 psig). The mixer power costs at 1.1¢/Kwh and a pump efficiency of 0.7 is as follows.

$$\text{Pumping costs (¢/1000 gal feed)} = 0.2\ X'_m \tag{34}$$

As several cases are examined, it will be seen that the pumping costs are very small compared to the ozone production costs.

Dissolved Ozone Distribution Ratio (S)

For a specified technical performance of an ozone wastewater treatment plant, the COD reaction rate correlation, Eq (13), yields only the time weighted average dissolved ozone concentration, Z^*_N, that is required. But even with Z^*_N specified, the values of Z_i for each of the N reactors may be varied subject only to the constraint of Eq (2) or Eq (3). Since the ozone dosage requirement, D_i, will generally be different for each of the reactors, there should be, for every combination of c_g and mixer sizes, one optimum Z_i distribution that yields a minimum total operating cost.

For the purposes of this discussion, only a linear distribution for equivolume stages will be considered.

$$Z_i = Z_1 + \frac{i-1}{N-1}(Z_N - Z_1) \tag{35}$$

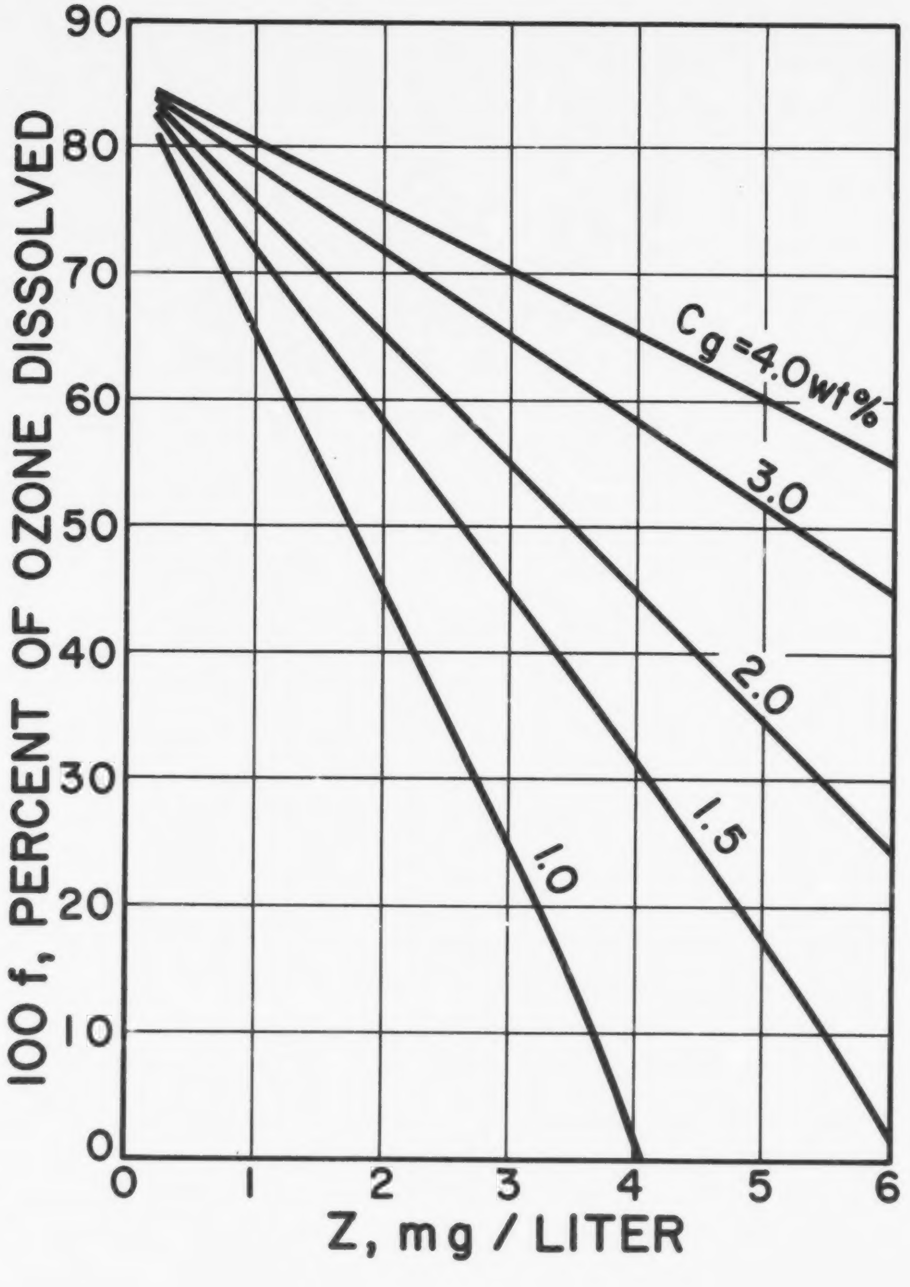

Figure 58. PERCENT OF OZONE FEED DISSOLVED IN TYPICAL MIXER

TABLE 15.

PERCENT OF OZONE FEED DISSOLVED IN TYPICAL MIXER

WT PCT	OUTLET DISSOLVED OZONE CONCENTRATION, MG/L												
OZONE	0.30	0.50	0.70	1.00	1.50	2.00	2.50	3.00	3.50	4.00	5.00	6.00	8.00
1.00	78.91	74.94	70.97	65.01	55.05	45.06	35.00	24.81	14.28	2.70	0.00	0.00	0.00
1.25	80.11	76.95	73.77	69.00	61.06	53.09	45.11	37.08	28.96	20.72	2.78	0.00	0.00
1.50	80.94	78.30	75.65	71.69	65.08	58.45	51.82	45.15	38.46	31.74	17.98	2.86	0.00
1.75	81.53	79.26	77.01	73.61	67.94	62.27	56.59	50.90	45.20	39.47	27.91	16.02	0.00
2.00	81.98	80.01	78.03	75.06	70.10	65.15	60.18	55.21	50.23	45.24	35.20	25.04	3.03
2.25	82.32	80.58	78.82	76.17	71.78	67.39	62.98	58.57	54.14	49.72	40.84	31.89	13.40
2.50	82.62	81.05	79.47	77.08	73.13	69.17	65.22	61.25	57.28	53.31	45.33	37.32	21.02
2.75	82.87	81.42	79.99	77.83	74.25	70.65	67.05	63.46	59.83	56.24	49.01	41.74	27.07
3.00	83.06	81.76	80.44	78.47	75.18	71.88	68.59	65.28	61.98	58.67	52.07	45.42	32.05
3.25	83.25	82.03	80.81	79.00	75.96	72.91	69.89	66.83	63.80	60.75	54.64	48.54	36.23
3.50	83.41	82.28	81.15	79.46	76.65	73.83	71.00	68.18	65.35	62.52	56.86	51.20	39.81
3.75	83.55	82.48	81.43	79.85	77.22	74.60	71.98	69.34	66.71	64.07	58.79	53.51	42.90
4.00	83.65	82.68	81.70	80.22	77.74	75.28	72.83	70.37	67.90	65.42	60.49	55.53	45.61

where Z_i is the outlet dissolved ozone from the

i-th stage in a N stage plant.

Each such linear distribution can be characterized by a distribution ratio.

$$S = Z_N/Z_1 \tag{36}$$

From Eq (35) and (36) and the rules for summing finite series, the following relations can be written for the i-th stage of a N stage plant.

$$Z_i = Z_N^*[1 + \frac{i - 1}{N - 1}(S - 1)]/[1 + 0.5\ (S - 1)] \tag{37}$$

$$Z_i^* = Z_N^*[1 + \frac{i - 1}{N - 1}(S - 1)/2]/[1 + 0.5(S - 1)] \tag{38}$$

Simultaneous Optimization of c_g, X_m', and S

On the basis of the estimated cost of ozone as a function of c_g, the mixer scaling correlation, and the linear dissolved ozone distribution, a procedure for simultaneously optimizing c_g, the mixer sizes, and the dissolved ozone distribution can be described.

Since not all of the plant operating costs will be influenced by the optimization procedure, it is convenient to divide the plant operating costs into three groups:

1. adjustable costs - - those costs strongly influenced by adjusting c_g, X_m', and S which are the total ozone generation costs and mixer pump power.
2. oxygen costs, and
3. nonadjustable costs - - the remaining operating costs which include labor, maintenance, overhead, and amortization and power costs for all equipment other than ozone generators, compressors, and dryers. (Mixer pump amortization is considered a nonadjustable cost, and pumping power adjustable.)

The optimization procedure described here is based on linear cost adjustments from the initial plant estimates. For these small adjustments of plant operating parameters, it is assumed that both the ozone production cost (¢/lb ozone) and the nonadjustable costs remain constant.

Certain overall plant parameters must be specified initially. These are feedwater flow, COD, and pH; product water COD, treatment time, and the number of reactors (N). From these parameters, the required value of D_N^* can be calculated from Eq (11), the required Z_N^* from Eq (12), and the value of X_p' from Eq (26).

From this point, the optimization procedure is doubly iterative in c_g and S as follows.

a. For a trial value of S in the first iteration, Z_i and Z_i^* values are obtained from Eq (37) and (38).

b. Applying Eq (12) or Fig 28 and 29 sequentially to the N reactors, the values of D_i^* are obtained for each reactor, and noting from Eq (7) that $D_i = D_i^* - D_{i-1}^*$, the values of D_i are calculated. The values of Q_i' can then be calculated from Eq (29) which for convenience can be placed on a 1000 gal basis as follows.

$$Q_i'(\text{lb } O_3/1000 \text{ gal}) = 0.00833\ L_f D_i \qquad (40)$$

c. In the second iteration for each assumed value of S, a value of c_g is assumed. For each reactor, the value of f_i for the trial values of c_g and Z_i is obtained from Table 15.

d. Taking (G/L) = 1, the value of X_m' for each stage is obtained from Eq (31).

e. The ozone feed to each stage is Q_i'/f_i, and the cost is calculated using Fig 57.

f. Pumping power costs for each stage are calculated from

Eq. (34)

g. The adjustable costs for each stage are the sum of items e and f.

h. The adjustable costs for the plant for the trial values of c_g and S are the sum of item g for the N stages in the plant.

The optimum values of c_g and S are those yielding the minimum costs in item h. The total operating cost is obtained by adding the oxygen cost and nonadjustable cost to the minimized adjustable costs. For a 10 Mgd plant, the oxygen costs are about as follows.

$$\text{Oxygen cost } (¢/1000 \text{ gal water}) = 0.0167(L_f - L_p + 40) \qquad (41)$$

Based on the initial cost estimates for a 10 Mgd plant, the nonadjustable costs are about 5¢/1000 gal water.

The overall fraction of ozone dissolved, f*, is as follows.

$$f^* = D^*_N L_f / F^*_N = \sum_1^N Q'_i \Big/ \sum_1^N (Q'_i/f_i) \qquad (42)$$

Specific Example

Continuing the example started in the discussion of the COD correlations, consider a 10 mgd plant receiving 40 mg/l COD at pH 7 with a desired reduction to 20 mg/l COD in 45 minutes in a three-stage plant. The required value of D* is 1.35 lb ozone dissolved/lb COD feed and Z* is 2.32 mg/l. X'_p is 126.3

Now to follow the procedure outlined above.

a. Assume S = 1.7

$Z_1 = 1.72$, $Z_2 = 2.32$, $Z_3 = 2.92$ mg/l

$Z^*_1 = 1.72$, $Z^*_2 = 2.02$, $Z^*_3 = 2.32$ mg/l

b. $D_1^* = 0.689$, $D_2^* = 1.033$, $D_3^* = 1.34$ lb O_3/lb COD feed

$D_1 = 0.689$, $D_2 = 0.344$, $D_3 = 0.305$ lb O_3/lb COD feed

$Q_1' = 0.230$, $Q_2' = 0.114$, $Q_3' = 0.102$ lb O_3/1000 gal feed

c. Assume $c_g = 2.0$ wt % ozone in oxygen.

From Table 16 for $c_g = 2.0$ and $Z_1 = 1.72$,

the value $f_1 = 0.679$ can be interpolated.

Similarly, $f_2 = 0.619$ and $f_3 = 0.559$.

d. From Eq (31) using G/L = 1, the values of X_m' are 1.53, 0.83, and 0.82 for mixers 1, 2, and 3, respectively. These values are well within the 0.54 to 2.75 range tested in the pilot plant.

e. The ozone production costs are 2.79¢, 1.52¢, and 1.50¢ per 1000 gal feed for stages 1, 2, and 3, respectively.

f. The water pumping costs are 0.31¢, 0.17¢, and 0.16¢ per 1000 gal feed for stages 1, 2, and 3 respectively.

g. The total adjustable costs for $S = 1.7$ and $c_g = 2.0$ wt % are 3.10¢, 1.69¢, and 1.66¢ per 1000 gal feedwater for stages 1, 2, and 3 respectively.

h. For all three stages, the total adjustable costs are 6.46¢/1000 gal feedwater.

The oxygen costs for this case are 1.00¢/1000 gal feedwater, one-third being due to COD reduction and two-thirds due to adding 40 mg/l dissolved oxygen to the wastewater. Adding this 1.00¢ and the 5¢/1000 gal for nonadjustable costs, the total treatment cost at $S = 1.7$ and $c_g = 2.0$ is 12.5¢/1000 gal treated. The value of f^* is 0.632.

The mixer sizes for the actual plant must be expressed as a scale factor applied to the pilot plant mixers. For stage 1, for example, $X_m'X_p' = 1.53 \times 126.3 = 193.2$. Thus the first stage mixer should have 193.2 times the rated capacity of the pilot plant mixer. This implies linear dimensions increased by the square root of 193.2 = 13.9. Naturally, a number of smaller mixers could be used. It is important to note, however, that the mixer size is rather critical; there is little leeway in specifying its size.

Values for the total adjustable costs for all three stages (item h) are shown in Table 16 for other assumed values of S and c_g. The minimum is at c_g = 2.5 wt % ozone and S =1.7. At these optimum conditions, the total treatment costs are about 6.38 + 1.00 + 5 = 12.4¢ per 1000 gal.

It is noteworthy that varying S at constant c_g produces an extremely shallow minimum in this case. In examining a number of other cases, the optimum value of S generally lies in the range 1 to 2. Therefore, the optimization procedure may generally be performed only for S = 1.7 with little error in the resulting minimum.

It is also important to note that the minimum obtained by varying c_g at constant S is not particularly sharp. Therefore, the exact c_g value selected is not very critical to plant economics.

Other Examples

In Table 17 are summarized the results of costs optimizations for a number of different plant specifications. All cases are for pH 7 feedwater. The total operating costs given are the sum of the adjustable costs, oxygen cost, and 5¢/1000 gal non-adjustable cost. The value f* is the fraction of the ozone feed to all stages that is dissolved. It bears repeating that these estimates are based on linear scaling from 10 mgd plant with ozone generator capacity of 7500 lb/day at 1.7 % ozone, and that in some of these examples,

Table 16.

VALUES OF ADJUSTABLE COSTS, ¢/1000 GAL, FOR EXAMPLE OZONE WASTEWATER TREATMENT PLANT

	c_g, Wt %					
S	1.7	2.0	2.5	3.0	3.5	4.0
1.0	7.06	6.60	6.49	6.81	7.44	8.37
1.3	6.92	6.50	6.41	6.74	7.38	8.31
1.7	6.89	6.46	6.38	6.71	7.35	8.28
2.0	6.92	6.47	6.38	6.72	7.35	8.28
2.5	7.00	6.52	6.41	6.74	7.37	8.29
3.0	7.11	6.59	6.45	6.76	7.39	8.31
4.0	7.34	6.73	6.54	6.83	7.45	8.37
6.0	7.71	6.97	6.69	6.94	7.55	8.46
7.5	7.92	7.10	6.77	7.01	7.60	8.51
10.0	8.19	7.27	6.88	7.09	7.67	8.58

the scaling is large.

Cases 1-5 show the effects of varying L_f at a required L_p of 20 mg/l in 45 min. The treatment costs increase rapidly with increasing L_f, and part of this very rapid increase is due to the smaller fraction of ozone dissolved.

Cases 6-8 show the effects of varying the number of stages while holding the treatment time constant. The effects are negligibly small.

Cases 2, 9, and 10 show the effects of varying the treatment time while holding other plant specifications constant. There is a reduction in treatment costs with increasing treatment time, and this reduction is due entirely to increased values of f*.

Comparisons of cases 10-14 with cases 1-5 show the effects of the longer treatment times for higher values of L_f. Here the effects are pronounced.

Cases 15-18 show the effects of decreasing the required product COD to 10 mg/l holding the treatment time at 45 min. Cost for more than 50% COD reduction is high.

Cases 19-22 compared to 15-18 show, again, the lower costs realized by extending the treatment time.

From all of the cases shown in Table 17 one point becomes clear; mixers of the type used in the pilot plant cannot economically handle high dissolved ozone requirements. This is not from a lack of mixing efficiency, but is a fundamental limitation of pure cocurrent mixing. For example, in a reactor operating at Z = 5 mg/l, a perfect cocurrent mixer

Table 17.

OPTIMUM PARAMETERS AND COSTS FOR VARIOUS PLANT SPECIFICATIONS

Case No.	Plant Specification, pH = 7.0 L_f mg/l	L_p mg/l	t^* Min	N Stages	Optimum Parameters S	c_g Wt %	Z^* mg/l	f^*	Total Operating Costs ¢/1000 Gal
1	30	20	45	3	2.0	2.0	0.98	.765	8.44
2	40	20	45	3	1.7	2.5	2.32	.679	12.37
3	50	20	45	3	1.7	2.5	3.49	.588	17.47
4	60	20	45	3	1.7	3.0	4.48	.569	23.78
5	80	20	45	3	1.3	3.0	6.04	.466	39.68
6	40	20	45	4	2.0	2.5	2.32	.68	12.36
7	40	20	45	6	2.0	2.5	2.32	.68	12.35
8	80	20	45	6	1.7	3.0	6.04	.470	39.42
9	40	20	90	3	2.0	2.0	1.25	.734	11.64
10	40	20	180	3	2.0	2.0	0.68	.789	11.33
11	30	20	180	6	2.5	2.0	0.28	.823	8.31
12	50	20	180	6	2.5	2.0	1.02	.756	14.69
13	60	20	180	6	2.5	2.0	1.31	.729	18.37
14	80	20	180	6	2.0	2.0	1.77	.685	26.48
15	20	10	45	3	1.7	2.5	3.95	.553	10.95
16	25	10	45	3	1.3	3.0	5.70	.489	15.47
17	30	10	45	3	1.3	3.5	7.09	.465	21.19
18	40	10	45	3	1.3	4.0	9.18	.413	36.08
19	20	10	180	6	2.5	2.0	1.15	.715	9.52
20	25	10	180	6	2.0	2.0	1.67	.696	11.84
21	30	10	180	6	2.0	2.5	2.08	.696	14.38
22	40	10	180	6	2.0	2.5	2.69	.650	19.80

would leave 1.2 % ozone in the vent gas.

It appears, then that cocurrent mixers such as were used in the pilot plant are best used at Z values of about 1 mg/l which can be realized by increasing the treatment time. Under such conditions, about 75% of the feed ozone would be dissolved.

If higher dissolved ozone values are required to attain higher reaction rates, then other types of mixers must be developed. They must embody some variant of gas-liquid counterflow, and the water entering the mixers must have a low dissolved ozone content. This would require a plant flow system completely different from the one used in the pilot plant.

Selection of Pretreatment

Any detailed cost effectiveness analysis of the myriad possible pretreatments that could be introduced before ozone tertiary treatment is entirely beyond the scope of this work. However, having found that the performance of the ozone process is apparently not dependent on the exact nature of the pretreatment, some guide in this area is available from the data in Table 17.

Attention is directed specifically to cases 10-14 and 19-22. These illustrate the approximate incremental cost reductions for ozone treatment that might be realized from the further removal of COD by a pretreatment process.

As an example, consider a plant requirement for 20 mg/l product COD and an initial feed COD of 60 mg/l. Assume that some pretreatment process under consideration could reduce the feed COD to 40 mg/l. Comparing case 13 with case

10, it can be seen that the savings in operating costs for ozone treatment would be 18.37 - 11.33 = 7.04¢/1000 gal. Therefore, if the pretreatment process being considered costs less than 7.04¢/1000 gal, it would be economically attractive.

It should be noted, though, that many of the possible pretreatment processes, in contrast to ozone treatment, simply separate the contaminants from the wastewater, and the costs of ultimate disposal of the concentrated wastes must be included in such economic comparisons of processes.

Comparison of Current Estimated Cost with Earlier Estimates

The cost estimates which are presented herein are based on the ozone treatment technology demonstrated in the pilot plant. The estimated cost for operation with an ozone feed to water ratio of 75 lb of ozone per million lb of wastewater is 12.4¢ per 1000 gallons for a plant with design capacity of 10 mgd.

In a previous contract for a laboratory investigation of wastewater treatment with ozone, the estimated cost for a large scale treatment plant was 7.7¢ per 1000 gallons (1). The higher estimated cost which is now presented is due, in the main, to an increase of over 30% in construction costs as shown by the EN-R cost index (20), an increase in electrical power cost from 0.8¢ to 1.1¢/Kwh, increased labor costs, and from change in scope of the plant design. The earlier estimate was based only on a projection of laboratory data.

SECTION X

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The cooperation of the firms mentioned below is gratefully appreciated in supplying cost information for commercial scale equipment.

It should be emphasized that mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Environmental Protection Agency.

Ozone Generators

*Crane Co., Cochrane Division
800 3rd Ave., P. O. Box 191
King of Prussia, Pa., 19406

W. R. Grace Co., Davison Chemical Div.
Charles and Baltimore Streets
Baltimore, Md. 21203

Pollution Control Industries
507 Canal Street
Stamford, Conn. 06902

*The Welsbach Corp.
Ozone Systems Division
3340 Stokley Street
Philadelphia, Pa. 19129

*Also supplied cost data for integrated oxygen recycle systems.

Gas Dryers

The C. M. Kemp Manufacturing Co.
Glen Burnie, Md. 21061

Kahn and Company, Inc.
885 Wells Road
Wethersfield, Conn. 06109

Pall Trinity Micro Corp.
Cortland, New York 13045

Recycle Blowers

North American Rockwell
Pneumatics Division
P. O. Box 2877 Commercial Station
Springfield, Mo. 65803

Injector-Mixers

Croll-Reynolds Co.
751 Central Avenue
Westfield, N. J. 07091

Penberthy Div., Houdaille Industries, Inc.
P. O. Box 112
Prophetstown, Ill. 61277

Liquid-Ring Compressors; Vacuum Pumps

Dresser Industries, Machinery Group
3201 Wolf Road
Franklin Park, Ill. 60131

Spray Nozzles

Spraying Systems, Inc.
3201 Randolph Street
Bellwood, Ill. 60104

Centrifugal Pumps

Buffalo Forge Co.
Pump Division
Buffalo, N. Y. 14205

SECTION XI

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SECTION XIII

GLOSSARY

TABLE OF SYMBOLS

a	Fitted coefficient, arbitrary subscripts
b	Slope of dosage curve, see Eq (8)
c	Weight percent ozone in oxygen
c_g	Weight percent ozone in oxygen from generator
c_v	Weight percent ozone in oxygen vented from reactor
D_i	Lb ozone dissolved in i-th reactor per lb COD in plant feedwater
D_N^*	Cumulative sum of D_i from first through N-th stage, See Eq (7)
DO_3	Dissolved ozone concentration in post-ozonation apparatus, see Fig. 3
d	$(P_1 - P_2)/P_2$, about 0.21 in pilot plant
e	Base of natural logarithms
F*	Ozone feed ratio, lb ozone generated/million lb water treated
f	Fraction of ozone feed to a mixer-reactor that is dissolved, see Eq (21)
f*	Fraction of total ozone feed to all stages that is dissolved, see Eq (42)
G_i	Gas flow rate to i-th mixer, SCF/hr
(G/L)	Volume ratio of gas to water feed to a mixer, SCF gas/cu ft water
g	Fitted coefficient in Eq (9)
H	Henry's Law solubility constant for ozone in water, mg/l/atm
h	Fitted coefficient in Eq (9)
j	Fitted coefficient in Eq (10)

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Kva	Electrical power to ozone generator in Kilovolt-amps calculated from voltmeter and ammeter readings
Kw_p	Electrical power to ozone generator, Kilowatts measured with integrating watt-hour meter
Kw_w	Electrical power to ozone generator, Kilowatts measured with electrodynamometer power meter
KW	Actual Kilowatts of mechanical power consumed by a mixer, combined water pumping power and gas compression power (appears only in combination T/KW)
k_1, k_2	First order COD reduction rate constant in "two-component" model, see Eq (5)
k_z	First order dissolved ozone consumption rate constant, see Eq (23)
L	COD concentration, mg/l
L_f	COD of feedwater entering ozone treatment plant, mg/l
L_p	COD of product water leaving ozone treatment plant, mg/l
Ln	Natural logarithm (to base e)
Log	Common logarithm (to base 10)
M_f	Lb/hr COD feed to plant
N	Number of stages or reactors in ozone treatment plant
n	Number of experimental data points in a statistical fit
n_c	Degrees of freedom removed by a statistical fit; generally, the number of coefficients fitted
P_1	Absolute pressure at mixer inlet, atm
P_2	Absolute pressure at reactor outlet, atm
Δp	Ozone partial pressure driving force between gas and liquid, atm; subscript 1 for mixer inlet, subscript 2 for reactor outlet, and subscript m for log mean of 1 and 2, see Eq (20)

Q	Lb ozone dissolved/hr, see Eq (29); or lb ozone dissolved/1000 gal water treated see Eq (40)
S	Dissolved ozone distribution ratio, see Eq (36)
s, s_e	Standard sample deviation, see Appendix 7
s_a, s_b, s_h	Standard deviation on a fitted coefficient, see Appendix 7
T	Transference of a cocurrent gas-liquid mixer of the type used in the pilot plant, see Eq (17), lb ozone dissolved/hr/atm mean partial pressure driving force
t^*	Cummulative ozone treatment time, hr
t_i	Treatment time in i-th reactor, hr
u	Fitted coefficient in Eq (10)
v_g	Volume fraction ozone in oxygen produced by generator
v_v	Volume fraction ozone in oxygen in spent gas vented from reactor
W_m	Water flow rate to mixer, gal/min
X'_p	Plant scaling factor, see Eq (26)
X'_m	Mixer scaling factor, see Eq (27)
x_1	Fraction of component 1 in "two component" model
$\bar{y}$	Calculated value of a general dependent variable, see Appendix 7
y	Experimental value of general dependent variable, see Appendix 7
Z_i	Dissolved ozone concentration at the outlet (top) of i-th reactor, mg/l
Z^*_N	Time weighted average of Z_i from first through N-th reactor

SUPERSCRIPTS

*	Time weighted average or cumulative variable
'	Parameter for large plant as distinguished from pilot plant parameter

SUBSCRIPTS

f	Feedwater
g	Ozone generator output
i	i-th of N reactors numbered sequentially from plant inlet
p	Product water
v	Spent gas from reactor

ABBREVIATIONS

BOD	Five-day biological oxygen demand
C	Feed pretreatment process, see Table 2
CL	Feed Pretreatment process, see Table 2
COD	Chemical oxygen demand
DC2	Feed pretreatment process, see Table 2
F	Feed pretreatment process, see Table 2
gpm	Gallons per minute
JTU	Jackson turbidity units
L	Feed pretreatment process, see Table 2
MC	Feed pretreatment process, see Table 2
Mgd	Million gallons per day
NH_3-N	Ammonia nitrogen
NO_2-N	Nitrite nitrogen
NO_3-N	Nitrate nitrogen
POA	Post-ozonation apparatus, see Fig 3
SCF	Standard cubic feet
SCFM	Standard cubic feet per minute
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon
UN	Pretreatment process, see Table 2
3B	Pretreatment process, see Table 2

SECTION XIV

APPENDICES

APPENDIX 1

DEVELOPMENT OF GAS-WATER MIXING SYSTEM

This section of the report summarizes experimental work which was done to optimize water-jet injectors as the primary gas-water mixing devices for the reactors of the Blue Plains pilot plant, as it had been shown in previous work that injectors had good potential for achieving effective mixing (1).

Based on the earlier work, it was concluded that six reaction vessels with a total residence time of about 60 minutes (at 35 gpm rate) should be used for the Blue Plains plant to provide flexibility in testing a variety of effluents with respect to both flow rate and level of contaminants. Previous results indicated that about five seconds contact time was needed in the vertical dissolver tube into which the injector discharged to obtain a high rate of transfer of ozone to the water (1).

A test unit was built and operated at the Research Laboratories of Airco, Inc., Murray Hill, N. J., for evaluating injector devices for mixing gas and water, simulating operating conditions which were expected for the Blue Plains pilot plant. A diagramatic sketch of the apparatus used for these evaluation tests is given in Figure 59. The water jet injector discharged into the top of a vertical glass pipe which is designed as the dissolver pipe. The end of this dissolver pipe was inserted through the top closure of a

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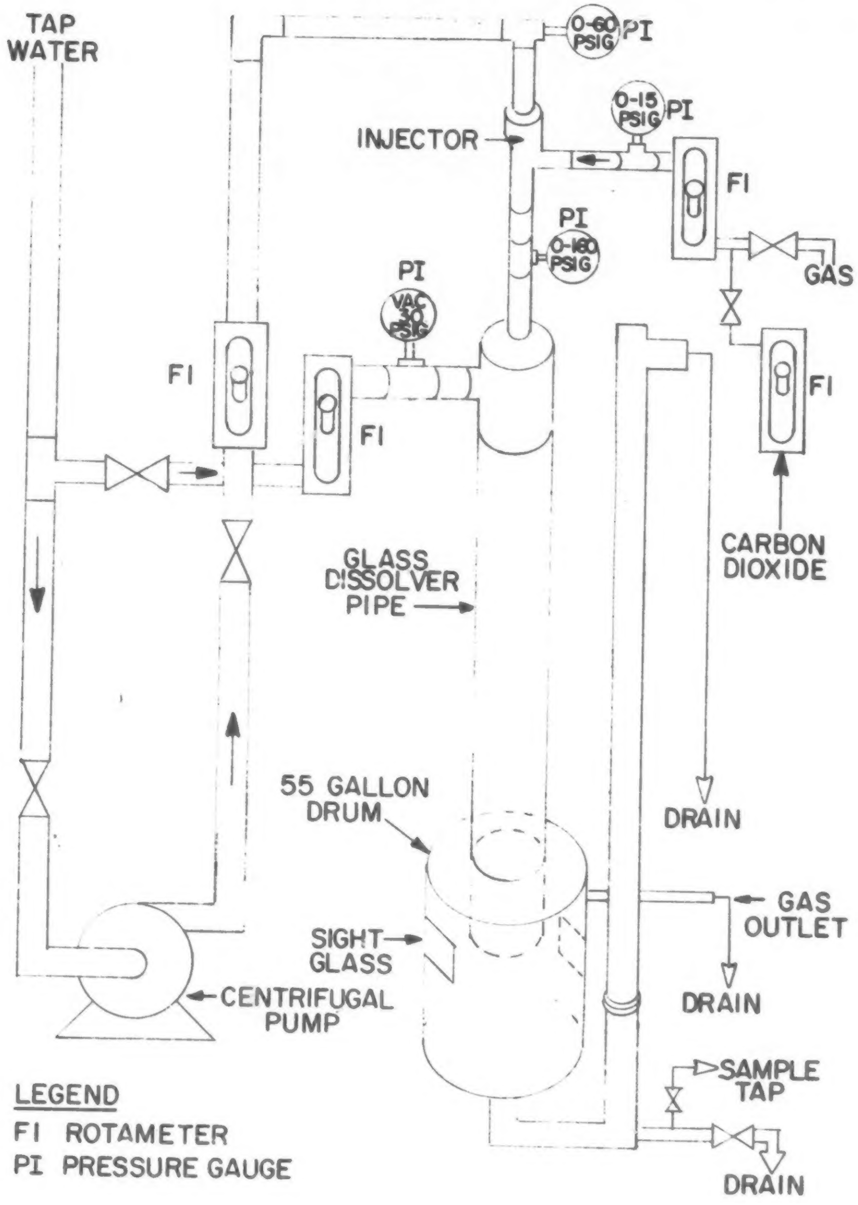
TAP WATER
0-60 PSIG
PI
INJECTOR
0-15 PSIG
PI
FI
PI
0-160 PSIG
GAS
PI
VAC 30 PSIG
FI
FI
FI
CARBON DIOXIDE
GLASS DISSOLVER PIPE
55 GALLON DRUM
DRAIN
GAS OUTLET
SIGHT GLASS
CENTRIFUGAL PUMP
DRAIN
SAMPLE TAP
DRAIN
LEGEND
FI ROTAMETER
PI PRESSURE GAUGE

Figure 59. INJECTOR TESTING APPARATUS

55-gallon drum and terminating about half-way inside the drum. A 1/2-inch diameter line carried off gas which rose to the top of the drum, along with a small amount of water. Most of the water was removed from the system through a 2-inch bottom outlet and into a section of pipe 20 feet high for maintaining a static head on the drum, equivalent to that expected for the pilot plant reactors. The gas bubbles which formed in the drum were observed through clear plastic windows.

Two sizes of dissolver pipes were used, namely 4-inch I.D. and 2-inch I.D. glass pipes, to show the effect of residence time in the dissolver tube. When the four-inch dissolver pipe was used, a glass tee was placed between the discharge of the injector and the top of the pipe into which an auxiliary stream of water was fed to achieve an extension of the turbulent mixing zone into the dissolver pipe. Various mixing and baffle arrangements were tested. The first injectors tested were standard PVC water-jet eductors used for vacuum service.

Operating data, consisting of liquid and gas flows, pressures, and stability of the liquid-gas mixtures in the dissolver pipe, were obtained. With certain combinations of nozzle and baffle arrangements and of fluid flow rates, the gas and liquid phases separated when the gas flow exceeded a certain rate. Various injector dispersion systems were tested over the same range of liquid and gas rates that were anticipated for the pilot plant.

An attempt was made to show the performance of the various dispersion systems by taking simultaneous high speed (1/50,000 sec.) photographs of the gas bubbles and of a transparent millimeter scale for estimating bubble size. Although these pictures permitted some approximate estimates of bubble surface, correlation with column performance was not possible. The photographic method is useful, however, in showing relatively large differences in dispersion systems.

Since the molecular weight of carbon dioxide is only 4 units smaller than ozone, and because of similar solubility values in water, we used CO_2 in lieu of ozone for obtaining mass transfer data for our dispersion systems. We assumed that these data represented to a reasonable degree the performance, except for the chemical reactions, that would be expected in the pilot plant using ozone. Carbon dioxide was used because we did not have an ozone generator of sufficient capacity.

For obtaining quantitative transfer data, CO_2 was titrated with 0.02 N sodium hydroxide by a standard method on water samples taken from the outlet of the absorber. Simultaneously saturation solubilities of the CO_2-air mixtures used were checked in a saturation apparatus attached to the system. These solubilities were found to check those given in the literature, using Henry's law. Tests were made in both 4-inch and 2-inch diameter columns to determine if column size was significant for performance of the dispersion systems. The operating characteristics of the injectors tested are given in Table 18.

The results from the mixing tests have been calculated in terms of mass transfer coefficient (Percentage of the cocurrent equilibrium concentration of dissolved CO_2 present in the water at the bottom of the tank.) and transfer rate per fluid horsepower. The mass transfer results for the CO_2 - air-water system are summarized in Table 19.

A special eductor which operated at a lower water-inlet pressure (30 psig at 35 gpm) gave the highest energy efficiency and just as high a mass transfer efficiency as the eductors which operated at 60 psig.

At low CO_2 dosages (less than 20 mg CO_2 per liter of water), a 2-inch dissolver column showed as high efficiency as a 4-inch column with a secondary shear zone. However, at higher dosages, the 4-inch tube with secondary liquid jets gives more mass transfer surface.

The nozzle of the 2-inch, high-pressure eductor was reamed out to reduce the inlet water pressure to about 30 psig. Energy efficiency was improved without impairing mass transfer efficiency.

From our test results, and from cost considerations, it was concluded that the eductors for the pilot plant should operate at a water feed pressure of less than 28 psig when the gas flow is about 8 scfm. A 2-inch dissolver tube could be considered as an alternative, particularly in the later stages where the ozone consumption is low.

The eductors ordered for the pilot plant were designed to reproduce the characteristics of the experimental model with polyvinyl chloride construction. The water feed pressure was lowered some more in these units. One of these units was set up on the injector testing apparatus with the proposed secondary water nozzle system. The final configuration of this system as installed in the pilot plant is shown in Figure 37.

In its operation, half the water flow is mixed with the gas stream in the eductor. This discharges through a short 2-inch

Table 18

SUMMARY OF PRESSURE vs.
FLOW CHARACTERISTICS OF INJECTORS

Injector	Water Flow Gal./Min	Water Pressure psig	Gas Flow scfm	Gas Inlet Pressure psig
A (1-1/2")	35	55	10	3
B (2") Stock Model	35	66	8	1.3
	25	37	11.4	5
	25	34	8	5
C (2") Modification of B	35	36	8	2
	25	22	8	2
D Special	35	30	11.4	5
	35	28	8	4
	25	14	8	4

Table 19

SUMMARY OF MASS TRANSFER TESTS

TEST GROUP NO.	1[(a)]	2[(a)]	3	4	5	6[(b)]
1. Make of injector	S-1	C-1	C-1	S-1	S-Z[(c)]	C-2
2. Diameter of dissolver pipe, in.	4	4	2	2	2	4
3. Water nozzle pressure of injector at 35 gpm flow - psig	60	30	30	60	32	20
4. Fluid power, input - horsepower per gpm flow at 35 gpm	0.018	0.021	0.019	0.033	0.017	0.012
5. Average percent of entering CO_2 transferred to water, experimental	60	60	45	39	49	56
6. Average percent of entering CO_2 transferred to water, calculated for cocurrent equilibrium	65	65	51	47	56	61
7. Average mass transfer efficiency $\frac{(5) \times 100}{(6)}$	91	91	89	83	87	92

(a) Secondary liquid jets used. Water flow to injector reduced to 30 gpm or less with total water flow at 55 gpm.

(b) Configuration used at pilot plant.

(c) Water nozzle enlarged to lower pressure.

pipe to the head of the 4-inch dissolver pipe, which carries the gas-liquid mixture to the bottom of the reactor tank. The other half of the water flow impinges upward and inward in two opposed flat jets against the descending gas-liquid mixture from the eductor discharge. This creates turbulence at the head of the dissolver pipe, concentrating most of the dispersion energy in this intimate mixture of gas and liquid as it descends to the bottom of the tank. The secondary liquid nozzles consist of stainless steel tubes passing horizontally on either side of the eductor discharge stream. These tubes are plugged at their inner ends. The water is discharged through 3/8 inch by 1-1/2 inch longitudinal slots which are faced inward and upward as shown. Flow passages into the mixing zone are well streamlined, so that unproductive friction and turbulence losses are minimized. The nozzle areas were sized small for the lower anticipated flows, with the intention of enlarging them later.

Column 6 of Table 19 shows the mass-transfer test results using the pilot plant system. It uses less power and gives mass transfer as good or better than any of the others. Feed pressures can be reduced further, particularly for injectors handling large recycle flows.

APPENDIX 2

OUTLINE SPECIFICATIONS OF MAJOR PILOT PLANT EQUIPMENT

Neutralization Tank. 4'-0" dia x 12'-2". Tank is constructed of mild steel. Inside of tank is protected with a cold application of an epoxy-bitumastic paint. Water capacity is 1200 gal.

Vacuum Deaerator. 30" O.D. x 36" to tangent lines. Tank capacity: 100 gal. Working pressure: 2 psia. Internal test pressure: 30 psig. Material of construction: ASTM A285, Grade C, flange steel. Inside coated with 6 mil layer of baked epoxy enamel.

Spray nozzle for water feed to the deaerator is a full cone center jet nozzle, No. 11-E, as supplied by Spray Engineering Co., New York, N. Y. 10036.

Vacuum Pump. A Nash pump, No. MD-15, 439-49015, in all-bronze construction, with a one HP motor was used.

Reactors (R-1 through R-6). 2'-0" I.D. x 20'-0" between bottom and top flanges. Shells are constructed of schedule 40 steel pipe. All interior surfaces of reactors are coated with 100 mils of a hot-applied Koppers 70-B bitumastic enamel.

Eductor Mixers. Details of the pilot plant eductor mixers are shown in Fig 37. The eductor, itself, is a Croll-Reynolds, 2-inch Aqua-Ductor fabricated in unplasticized polyvinylchloride to resemble No. 22 Aqua-Vactor.

Holding Tank. 6'-0" O.D. x 10'-0" high. This tank is constructed of mild steel with flat bottom and a cone roof. The interior walls are protected with a solvent type bitumastic coating, applied in the field.

Tank capacity to operating level is 2000 gal.

Pumps (P-1 through P-7). These pumps are Dean Brothers, Model D1206 inline centrifugal pump of 316 stainless steel construction for all wetted parts and fitted with John Crane mechanical seals.

Pump P-1 has a 3600 rpm, 5 h.p. electric motor. The rest of the pumps are equipped with 3600 rpm, 3 h.p. motors.

Ozone Generator. This unit was supplied by the Welsbach Corporation, Philadelphia, Pa., 19129. It is their model C1-34-D19L and has a rated capacity of 60 pounds per day of ozone from oxygen at 70°F and with a dew point of -60°F. The unit consists of the generator, transformer, variable transformer and operating controls. Material of construction is 304 stainless steel for all surfaces in contact with ozone. Gaskets are made of "Hypalon" (a chlorosulfonated polyethylene).

Absorption Dryer. The dryer is a package unit with filters, blow-off valve, instruments and controls. It was supplied by Gas Drying, Inc., Wharton, N. J., and is their Type V "Dehyditrol" size 60 unit. The desiccant is activated alumina.

Oxygen Compressor. Nash Engineering Co. Model AL-673, water ring compressor. Capacity: 50 scfm of oxygen at outlet pressure = 55 psig, saturated with water at 70°F. Inlet pressure 0 to 5 psig. All wetted parts of the compressor are 316 stainless steel. Unit operates at 3500 rpm and requires 21 brake horsepower.

Ozone Decomposer. This unit is Chromalox Model GCH-330 circulation electric heater, with AR type thermostat as manufactured by Edwin L. Wiegand Co., Clifton, N. J. 07013. The heater unit has 3 kilowatts capacity.

APPENDIX 3

CORROSION TESTS

Corrosion test specimens were placed in the product water holding tank at the water-gas interface near the effluent overflow. The following metals were tested: Stainless steel types 302, 304, 316, 409, 430; Incoloy alloy 800, Incoloy alloy 825, Carpenter stainless steel 20 Cb-3; aluminum 6061; high-strength low alloy steel Cor-Ten, and carbon steel. The temperature of the water during the test ranged from 65-75°F. The total time of the test was 105 days.

Corrosion rates, expressed as inches penetration per year, were less than 0.00001 for the stainless alloys, except a type 304 sensitized type which was 0.00003 in./yr. The rate of Incoloy 800 and 825, and Carpenter 20 Cb-3 were also less than 0.0001 in./yr. Aluminum 606 had a corrosion rate of 0.004 in./yr. High-strength, low alloy Cor-Ten steel and ordinary mild carbon steel had rates of 0.0125 and 0.0129 in./yr., respectively. In general, the stainless alloys showed up well in the test. Slight local corrosion was observed with Carpenter 20 Cb-3 and with sensitized type 304 stainless. This latter effect indicates that type 304 stainless, which is intended for welding or heat treatment, should be the low carbon type 304L. Although aluminum 6061 had a low weight loss rate, it did show rather deep pitting. Carbon steel and the high-strength, low alloy Cor-Ten corroded generally at an undesirably high rate and with no significant difference between them.

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APPENDIX 4

COPY OF SAFETY INSTRUCTIONS ISSUED TO PILOT PLANT PERSONNEL

General Outline

Oxygen and ozone are used in the pilot plant for treatment of secondary effluents from wastewater treatment plants. Ozone is made from pure oxygen gas by its reaction in an electrical discharge. A mixture of ozone in oxygen results - the maximum concentration of ozone will be about 3%. Both oxygen and ozone have properties which differ considerably from air and, consequently, practices and work habits will differ from those when working with air. The purpose of this safety section is to discuss and itemize the safe practices to be followed in the pilot plant.

Properties of Oxygen

Oxygen is a colorless, odorless and tasteless gas at atmospheric temperatures and pressures. About one-fifth of the atmosphere is oxygen. Oxygen will combine, either directly or indirectly, with almost all other chemical elements. This outstanding property enables it to sustain life and to support combustion. Although oxygen itself does not burn, materials which burn in air will burn much more vigorously and at a higher temperature in oxygen. Grease and oil become highly flammable in the presence of oxygen and must not be allowed to contaminate oxygen piping or equipment.

Since oxygen is an invisible gas, it is impossible to see an oxygen enriched atmosphere; therefore, good housekeeping is essential. Storage of combustible materials is not permitted in areas where oxygen enriched atmospheres could exist. For the same reason, vessels and other equipment must be purged

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with air until a normal oxygen-in-air concentration is reached before repair work is started. In addition, general ventilation of the building must be in operation to remove any local concentrations of oxygen.

Retention of gas within a container at a pressure higher than the design pressure of the container can be dangerous whether it is oxygen or air. However, it is standard industrial practice to prevent excessive pressure by use of relief devices to maintain pressures at a safe level.

Properties of Ozone

Ozone, O_3, is an unstable, blue gas with a pungent characteristic odor. It is generally encountered in dilute form in a mixture with air or oxygen. The color is not noticeable at the concentrations used in wastewater treatment.

Ozone is a very powerful oxidizing agent in both inorganic and organic systems. Ozone is much more reactive than oxygen. This strong oxidizing property of ozone is utilized in the wastewater treatment process.

Toxicity of Ozone

The maximum allowable concentration of ozone for continuous exposure is 0.1 part per million. Since toxicity is a result of ozone concentration and time of exposure, higher concentrations can be tolerated for a short time. An exposure to one part per million for 10 minutes is considered non-toxic by health authorities.

Oxygen, Ozone and the Oxidation Process

Pure oxygen is piped into the building from two liquid oxygen supply tanks which are located on a pad along the north side of the building. Oxygen is fed automatically under controlled pressure of 10 to 15 psig into the oxygen recycle system. The oxygen feed plus the oxygen that is being recycled pass into an electrical device for the generation of ozone. A mixture of ozone (1 to 3%) in oxygen is produced. This gas mixture is used to treat the wastewater in six reactor columns.

Any gas that is released from the recycle system is passed through an electric furnace at 600°F in which any residual ozone is destroyed before it can be discharged into the atmosphere.

Building Ventilation and Air Monitoring

The two roof exhaust fans are operated when the plant is operating. These fans have capacity to completely change the air of the building every 6 minutes. An ozone analyzer is provided for measuring ozone concentrations of the building air. In addition to the analyzer, the human nose is probably the most sensitive analyzer of all for detection of ozone. Unpleasant sensations will most likely develop before dangerous levels of ozone are reached.

Emergency Conditions

The pilot plant for ozone treatment of wastewater is well designed and every attempt was made to use the best equipment available for the job. Safety of personnel was a prime consideration in the design. Nevertheless, in the event that an unforeseen mishap occurs, shut down the ozone generator in the following sequence:

1. Push the STOP buttons.
2. Turn off cooling water.
3. Allow dry air or oxygen to pass through the ozonator for 15 to 20 minutes before the generator outlet valve is closed.

Correct any unsafe condition that may have developed before starting the ozonator again and resuming normal operation.

Minimal Safety Rules and Practices for Operators of the Ozone Treatment Process

1. Do not Smoke in the main equipment area. Smoking is permissible in the control room - but here, too, care should be taken to keep away from oxygen streams that are being analyzed.
2. Cleanliness and good housekeeping are essential. Do not wear dirty or greasy work clothing or gloves. Do not store combustibles in the pilot plant area.
3. Check all safety devices periodically; be sure that cooling water flows to the ozonator, the oxygen compressor, vacuum pump and all seals are at the proper level.
4. Make certain the ventilating system of the building is operative. In case of leakage or suspected oxygen gas leakage, ventilate the building by opening all doors to dilute the oxygen concentration. Inform the Supervisor of the leak.
5. Do not perform any repair work on equipment without permission of the Supervisor. Any repair work on the Kryo-Flow oxygen system will be performed by the supplier.
6. Use only the recommended pipe fitting compounds and gaskets on the oxygen lines.
7. Never use oxygen as a substitute for compressed air.
8. Read the instruction manuals pertaining to each mechanical piece of equipment for proper handling of these items.
9. Know where the emergency shut-off valve for the oxygen supply is located.

APPENDIX 5

ANALYTICAL PROCEDURES

The analytical methods used were adapted from "Standard Methods for the Examination of Water and Wastewater"(5) and from "FWPCA Methods for Chemical Analysis of Water and Wastes"(4).

Chemical Oxygen Demand (COD) (Low Level)

In the previous prepilot work on ozone treatment, monitoring of the pollutant removal was done by measuring COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon)(1). At first, measurement of TOC was favored because it was a rapid instrumental analysis and seemed to give satisfactory results. Analysis for BOD_5 was much too slow and cumbersome to supply the large number of analyses, and also there was some question as to the accuracy of BOD analyses when applied to water in which the organic substrate had been radically altered by ozone treatment.

When low pollutant levels were reached in the ozone treatment, reading of the TOC analyzer recorder charts became difficult, and trouble was encountered in the electronic systems. TOC also tended to approach COD in numerical value in the neighborhood of 8 mg/l, indicating that carbon dioxide (the substance measured in the TOC analyzer) was being evolved from inorganic bicarbonates and sesquicarbonates along with organic sources of extra CO_2.

Therefore, in the Blue Plains pilot plant work, main reliance was put on COD analyses, starting with the low-level procedure given in the FWPCA methods manual (4).

The first effluents treated involved very low levels of COD (4 to 20 mg/l). Extreme precautions were required to get consistent, replicate results. It was found that distilled water from the laboratory stills was not of consistently good quality. A bottled, pyrogen-free distilled water was substituted, which improved the reproducibility of the results somewhat. Great care was taken in cleaning all glassware and sample bottles with chromic acid cleaning solution, rinsing with good distilled water, and providing protection from contamination during sampling and analysis.

Another source of error with the standard procedure was found as a result of receiving an unusually bad bottle of mercuric sulfate. In the usual procedure, this is added to the sample as a powder. Unbelievably erratic results were obtained when use of this lot of mercuric sulfate was started. The trouble was traced to the presence of non-uniformly distributed organic dirt in the reagent. Since dirt is always present to some extent in reagents, dry powders should not be added to these samples. One small particle of dirt weighing as little as 0.1 mg can cause a gross error at the very low COD levels. The procedure was modified to introduce all reagents in solutions. In this way, any organic contaminant can be corrected by the blanks which are run with each batch of samples.

The standard low level COD procedure calls for the dissolution of 1 gm of mercuric sulfate in 5 ml concentrated sulfuric acid in each reflux flask followed by the addition of 25 ml of 0.025 N potassium dichromate. In the modified procedure, these reagents were combined into one solution as follows. 80 gm of mercuric sulfate was dissolved in 100 ml conc. sulfuric acid diluted with 900 ml water. To this solution was added 300 ml conc. sulfuric acid and 500 ml of

0.1 N potassium dichromate solution, and the results were diluted to 2000.0 ml. After filtering and aging for about a day, it was then cross-standardized against straight 0.025 N potassium dichromate using ferrous ammonium sulfate. To each reflux flask, 25 ml of the modified solution was added, and from that point, the analysis followed the standard procedure.(4)

Ozone in Gas

Ozone in oxygen was determined by the standard iodometric method (5). For application to our system, the gas sample was passed through a gas washing bottle with a fritted glass sparger containing 300 ml of water and 100 ml of 10% KI solution. The gas discharge was measured in a wet-test meter. Usually the sample volume was 1/2 cubic foot. A 25 ml aliquot was pipetted from 400 ml of KI solution, 25 ml of 10% sulfuric acid and 50 ml of distilled water were added, and the aliquot titrated with 0.1 N thiosulfate solution which was standardized daily.

When there was difficulty in getting a 0.5 cu ft gas sample, the sample volume was reduced to as little as 0.1 cu ft with a corresponding increase in the aliquot taken.

The absorption was checked by running two absorbers in series and virtually no iodine was ever liberated in the second absorber.

Ozone Dissolved in Water

To determine dissolved ozone in water, the liquid sample was taken in a 500 ml glass graduated cylinder. First, 80 ml of 10% KI solution and 10 drops of 5% KOH solution were put in the cylinder. The sample line was then purged, and the cylinder was filled as rapidly as possible to the 480 ml mark with sample, taking care to keep the tip of the sample tube near the surface of the liquid in the cylinder. The contents of the cylinder were shaken; then 20 ml of 10% sulfuric acid was added. The entire contents of the cylinder was titrated with the 0.1 N thiosulfate solution, using starch indicator added near the end point.

As mentioned in the reference (6) the reaction between ozone and KI to liberate iodine must take place at a pH of 9.5 or higher in order to obtain accurate results. The titration with thiosulfate, however, must be done in acid solution, hence the acid addition must be made just before the titration.

Oxygen Content of the Recycle Gas

Oxygen analyses were made on samples obtained from the gas feed stream to the ozone generator.

The oxygen content of the gas stream was determined by saturating distilled water in a flow cell with the gas. This cell contained the probe of a Precision No. 68859 Galvanic Cell Oxygen Analyzer. The oxygen concentrations indicated for samples obtained from the gas sample outlet were compared with results for streams of pure oxygen and of air. Readings were taken from these three streams in succession at least three times and were averaged for each stream. The ratio of the average readings of the sample and of pure oxygen times 100 gives the percent oxygen in the recycle stream.

In addition, several analyses of the gas were made with a conventional Orsat apparatus to measure oxygen, carbon dioxide and inerts (assumed to be nitrogen).

Turbidity

Turbidities were determined on incoming and ozone treated water with a Hach Model 2100 turbidimeter. This is a nephelometer which reads directly in Jackson Turbidity Units (JTU).

pH

Values of pH were measured with a Hach Model 2075-00 glass electrode pH meter, which was calibrated each shift with standard buffer solution.

Other Analyses

For part of the operating period, special samples were collected in the early morning and taken immediately to the EPA analytical laboratory at Blue Plains for BOD, TOC, and ammonia, nitrite, nitrate and Kjeldahl nitrogen analyses.

Samples of untreated feed were taken before and after vacuum deaeration, in a few runs.

The samples were all run by the standard methods used in the EPA laboratory.

The BOD values are subject to some question because of the peculiar behavior of ozone-treated water in the BOD determination.

APPENDIX 6

PLANT PROFILE DATA SETS

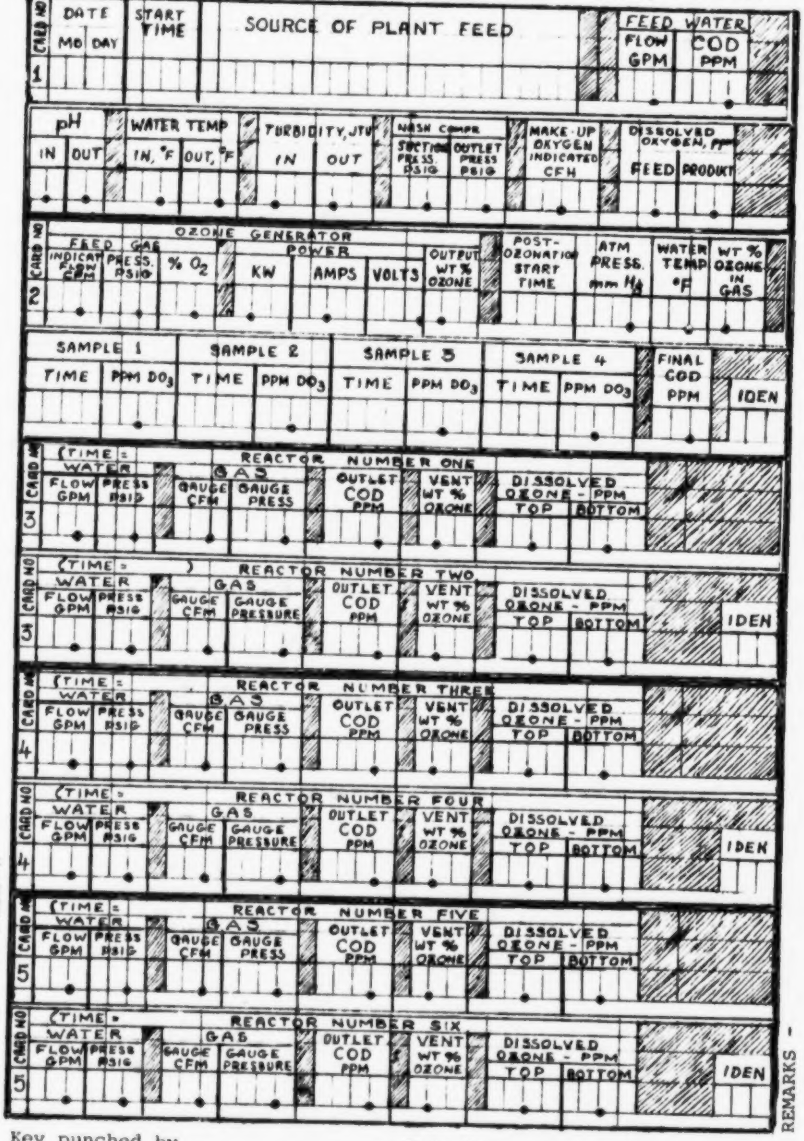
During normal pilot plant operations, a complete plant profile data set was collected once each eight-hour shift. These data sets included the necessary data for evaluating the COD reduction, ozone consumption, mechanical and electrical work expended, etc. for each stage of the plant. In addition to being recorded in plant logs and laboratory notebooks, these data were also entered onto a special data sheet by the plant operators and the chemical analyst.

A copy of the actual data sheet used is shown on page 211. It is laid out to facilitate key punching of the data onto five IBM computer cards for subsequent computer processing. Each block on the data sheet corresponds to a column on a standard IBM card. Most of the entries are self-explanatory. The latter columns for card 2 are for data from the post-ozonation experiment. The blocks "IDEN" are for a numeric code designating the shift and date. The "time" blank for each of the six reactors (not key punched) is the time at which each sample for COD analysis was taken; these were selected according to the feedwater flow rate to approximately follow a slug of water through the train of reactors. All entries are fixed format numeric except for "Source of Plant Feed" which is encoded alphanumerically.

Following the copy of the data sheet is a tabulation of all the complete plant profile data sets collected in the course of this investigation. Only the independent plant parameters and the final COD are listed. Not included in these tables are the numerous other data sets showing only plant inlet and outlet conditions.

The tabulation is arranged chronologically, and it is subdivided according to feedwater pretreatments. The column headings are, for the most part, self-explanatory. Times are on the 2400 basis. Feedwater GPM (gal/min) values are the net feeds to the plant. Under the "ozone generator" heading, "PCT" refers to the weight percent ozone produced by the ozone generator, and "KW" refers to the actual kilowatts of electrical power drawn by the generator corrected to the watt-hour meter basis. Entries in which both water and gas flows to a mixer are shown as zero indicate that the mixer was not being used.

REACTOR PROFILE DATA SHEET
Airco Ozone Water Treatment Pilot Plant - Washington, D.C.



CARD NO	DATE		START TIME	SOURCE OF PLANT FEED	FEED WATER	
	MO	DAY			FLOW GPM	COD PPM
1						

pH		WATER TEMP		TURBIDITY, JTU		NASH COMPR		MAKE-UP OXYGEN INDICATED CFH	DISSOLVED OXYGEN, PPM	
IN	OUT	IN, °F	OUT, °F	IN	OUT	SUCTION PRESS PSIG	OUTLET PRESS PSIG		FEED	PRODUKT

CARD NO	OZONE GENERATOR							POST-OZONATION START TIME	ATM PRESS. mm Hg	WATER TEMP °F	WT % OZONE IN GAS
	FEED GAS			POWER			OUTPUT WT % OZONE				
	INDICAT FLOW CFM	PRESS. PSIG	% O_2	KW	AMPS	VOLTS					
2											

SAMPLE 1		SAMPLE 2		SAMPLE 3		SAMPLE 4		FINAL COD PPM	IDEN
TIME	PPM DO_3	TIME	PPM DO_3	TIME	PPM DO_3	TIME	PPM DO_3		

CARD NO	(TIME =		REACTOR NUMBER ONE					
	WATER		GAS		OUTLET COD PPM	VENT WT % OZONE	DISSOLVED OZONE - PPM	
	FLOW GPM	PRESS PSIG	GAUGE CFM	GAUGE PRESS			TOP	BOTTOM
3								

CARD NO	(TIME =)		REACTOR NUMBER TWO						
	WATER		GAS		OUTLET COD PPM	VENT WT % OZONE	DISSOLVED OZONE - PPM		IDEN
	FLOW GPM	PRESS PSIG	GAUGE CFM	GAUGE PRESSURE			TOP	BOTTOM	
3									

CARD NO	(TIME =		REACTOR NUMBER THREE					
	WATER		GAS		OUTLET COD PPM	VENT WT % OZONE	DISSOLVED OZONE - PPM	
	FLOW GPM	PRESS PSIG	GAUGE CFM	GAUGE PRESS			TOP	BOTTOM
4								

CARD NO	(TIME =		REACTOR NUMBER FOUR						
	WATER		GAS		OUTLET COD PPM	VENT WT % OZONE	DISSOLVED OZONE - PPM		IDEN
	FLOW GPM	PRESS PSIG	GAUGE CFM	GAUGE PRESSURE			TOP	BOTTOM	
4									

CARD NO	(TIME =		REACTOR NUMBER FIVE					
	WATER		GAS		OUTLET COD PPM	VENT WT % OZONE	DISSOLVED OZONE - PPM	
	FLOW GPM	PRESS PSIG	GAUGE CFM	GAUGE PRESS			TOP	BOTTOM
5								

CARD NO	(TIME =		REACTOR NUMBER SIX						
	WATER		GAS		OUTLET COD PPM	VENT WT % OZONE	DISSOLVED OZONE - PPM		IDEN
	FLOW GPM	PRESS PSIG	GAUGE CFM	GAUGE PRESSURE			TOP	BOTTOM	
5									

REMARKS -

Key punched by ____________ Data by ______________________

Table 20 - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- 3-STAGE BIOLOGICAL + LIME + FILTER (3B+L+F)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
2/ 1	1000	20.0	8.6	48.4	22.0	1.94	3.2	20/1.9	55/1.8	55/1.8	55/0.9	55/0.9	54/0.9
2/ 2	1000	14.0	8.7	34.6	13.0	2.12	3.1	14/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/ 3	1600	22.0	9.1	52.8	26.5	2.18	3.1	22/1.8	55/1.8	54/1.8	54/0.9	54/0.9	54/0.9
2/ 4	1700	24.0	8.9	52.8	12.5	2.04	2.9	24/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/ 5	1700	22.5	8.8	69.0	22.0	2.02	3.0	22/1.8	55/1.8	55/0.9	55/0.9	54/0.9	55/0.9
2/ 8	2000	21.5	9.6	67.6	48.6	1.70	2.8	21/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/ 9	2000	18.0	9.3	45.6	17.7	2.86	4.4	18/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/10	2000	19.0	9.2	22.9	5.3	2.79	4.4	19/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/11	2000	19.0	9.4	16.5	7.0	2.79	4.4	19/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/12	2000	18.0	9.2	19.2	9.3	2.03	3.1	18/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/16	2000	20.0	8.5	16.2	6.1	1.86	3.3	20/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/17	2000	22.0	9.2	15.0	3.5	2.24	3.2	22/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/18	1000	12.0	9.3	15.0	4.2	1.95	2.8	12/1.8	55/1.8	55/1.8	55/0.9	55/0.9	55/0.9
2/19	0	17.5	9.8	13.5	6.2	1.20	2.9	17/2.7	55/2.7	55/2.7	55/2.7	55/2.7	55/2.7
2/22	2000	17.5	7.6	13.3	8.2	1.08	2.9	17/2.7	55/2.7	55/2.7	55/2.7	55/2.7	55/2.7
2/23	2000	22.0	7.1	12.8	5.3	1.11	2.8	22/2.7	55/2.7	55/2.7	55/2.7	55/2.7	55/2.7
2/25	2000	24.0	7.3	16.0	8.2	1.04	2.7	24/2.7	55/2.7	55/2.7	55/2.7	55/2.7	55/2.7
3/ 1	1600	28.0	7.5	9.7	1.6	1.73	2.7	28/1.8	55/1.8	55/1.8	54/0.9	55/0.9	55/0.9
3/ 2	1600	27.5	7.1	18.1	10.3	1.56	2.8	27/0.9	55/2.8	55/1.4	55/0.9	56/0.9	55/3.2
3/ 3	1600	30.0	7.3	13.3	6.8	1.54	2.8	30/0.9	55/2.8	55/1.4	55/0.9	55/0.9	55/3.4
3/ 4	1600	30.0	7.6	54.0	22.4	2.53	6.7	30/0.9	55/3.2	55/1.4	55/1.8	55/1.8	55/1.8
3/ 5	1600	30.0	7.3	65.0	39.8	2.46	6.9	30/1.8	55/3.2	55/2.3	55/1.8	55/1.8	55/1.8
3/ 9	1600	16.0	7.6	89.2	27.4	2.81	8.4	16/1.9	56/3.2	55/2.3	55/1.8	55/1.8	55/1.8
3/11	1600	21.0	6.6	68.6	19.6	2.13	8.6	21/3.6	55/4.5	53/3.6	55/1.8	55/1.8	55/1.8

(CONTINUED)

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- 3-STAGE BIOLOGICAL + LIME + FILTER (3B+L+F)
(CONTINUED)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
3/12	1600	21.0	7.4	112.0	49.6	2.04	8.7	21/3.6	55/4.5	55/3.6	55/1.8	55/1.8	55/1.8
3/15	2000	20.0	7.4	57.2	6.0	2.30	8.6	20/3.6	55/4.5	55/3.6	55/1.8	55/1.8	54/1.8
3/16	2000	20.0	7.1	13.6	4.8	0.97	2.8	20/3.2	55/2.7	55/2.3	55/1.8	55/1.8	55/1.8
3/17	2000	20.0	7.4	10.0	4.3	1.10	2.8	20/3.2	55/2.7	55/2.3	55/1.8	55/1.8	55/1.8
3/18	1700	21.0	7.8	12.1	8.6	1.13	2.8	21/3.2	55/2.7	55/2.3	55/1.8	55/1.8	55/1.8
3/22	2000	20.0	7.5	11.4	0.4	0.86	1.4	20/2.7	55/4.6	56/2.7	55/0.4	55/0.0	0/0.0
3/23	2000	20.0	8.2	12.2	7.3	0.86	1.4	20/2.7	55/4.6	55/2.7	55/0.4	55/0.0	0/0.0
3/24	2000	20.0	8.2	13.0	6.2	0.85	1.4	20/2.8	55/4.6	54/2.8	55/0.4	56/0.0	0/0.0
3/25	2000	21.0	7.3	13.0	10.8	0.94	1.4	20/2.8	55/4.6	55/2.8	55/0.4	55/0.0	0/0.0
3/26	2020	20.0	7.4	4.3	3.2	0.86	1.4	20/2.7	55/4.6	55/2.7	55/0.4	55/0.0	0/0.0
3/31	1920	20.0	7.6	10.6	0.1	0.77	1.5	20/3.7	55/4.6	53/3.7	54/1.8	55/0.9	54/0.9
4/ 1	1820	20.0	8.0	10.4	7.3	1.10	1.5	20/1.8	55/2.8	54/1.8	57/0.9	55/0.9	55/0.9
4/ 2	800	20.0	8.0	12.2	6.8	1.03	1.4	20/1.8	55/2.8	55/1.8	55/0.9	55/0.9	55/0.9
4/ 5	1920	21.0	5.6	13.3	9.9	1.01	1.6	21/1.4	55/2.8	55/1.4	55/0.9	55/0.9	55/0.9
4/ 6	1920	21.0	5.6	12.1	8.3	1.36	1.5	20/1.4	55/2.8	55/1.4	55/0.9	55/0.9	55/0.9
4/ 9	1920	22.0	5.4	10.4	9.0	1.29	2.1	44/1.3	55/2.7	56/1.3	55/0.9	55/0.9	55/0.9
4/12	1920	21.0	8.5	11.1	4.8	1.16	1.8	51/1.4	55/2.8	55/1.4	55/0.9	56/0.9	55/0.9
4/13	1920	22.0	8.3	10.9	5.9	1.39	2.0	51/1.4	55/2.8	55/1.4	55/0.9	55/0.9	56/0.9
4/14	2000	18.0	8.3	19.0	8.5	1.09	1.6	54/1.4	55/2.8	55/2.3	55/0.9	55/0.9	55/0.9
4/15	1920	20.0	8.3	20.1	7.6	3.08	6.7	52/1.8	55/2.8	55/1.4	55/0.9	55/0.9	55/0.9
4/16	1900	20.0	8.3	14.0	7.1	1.16	2.5	52/1.4	55/2.8	55/1.4	55/0.9	55/0.9	55/0.9
4/19	1920	21.0	8.2	19.2	7.1	1.55	2.8	53/3.7	55/2.7	54/1.8	55/0.9	55/0.9	55/0.9
4/20	1920	21.1	8.0	7.6	7.1	1.06	1.8	52/3.2	55/2.7	55/1.3	55/0.9	55/0.9	55/0.9
4/21	1920	21.4	8.1	12.4	8.0	1.22	2.1	53/3.2	55/2.7	55/1.3	55/0.9	55/0.9	55/0.9

(CONTINUED)

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- 3-STAGE BIOLOGICAL + LIME + FILTER (3B+L+F)
(CONTINUED)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
4/22	1920	21.5	6.6	11.1	4.5	1.24	2.1	53/3.2	55/2.7	55/1.3	55/0.9	55/0.9	62/0.9
4/23	1920	21.5	8.1	15.1	6.8	1.22	2.1	53/2.9	55/2.7	55/1.3	56/0.9	55/0.9	62/0.9
4/26	1920	21.5	7.8	13.7	7.6	1.24	2.1	55/3.2	53/2.7	56/1.3	55/0.9	56/0.9	62/0.9
4/27	800	22.0	7.5	13.0	6.3	1.11	2.2	54/3.2	55/2.7	55/1.3	55/0.9	55/0.9	63/0.9
4/27	1920	21.5	8.0	13.0	6.9	1.64	2.1	55/3.2	56/2.9	55/1.3	55/0.9	56/0.9	63/0.9
4/29	800	22.0	8.0	14.2	7.1	1.18	2.2	54/3.2	56/2.7	55/1.3	55/0.9	55/0.9	63/0.9
4/28	2130	21.5	8.1	17.0	10.6	1.28	2.1	55/3.2	54/2.9	54/1.3	55/0.9	55/0.9	61/0.9
4/29	1920	21.5	8.8	16.5	8.2	1.68	2.8	55/3.2	55/2.7	55/1.3	55/0.9	55/0.9	65/0.9
5/ 3	1920	21.5	8.5	21.2	6.5	1.59	2.9	52/3.2	55/2.7	55/1.3	55/0.9	55/0.9	63/0.9
5/ 4	1920	22.3	9.6	23.8	9.3	1.52	2.8	52/3.2	55/2.7	55/1.3	55/0.9	55/0.9	62/0.9
5/ 5	1920	21.5	9.8	41.2	10.9	3.41	7.0	52/2.8	55/1.4	55/0.9	55/0.9	55/0.9	62/0.9
5/ 6	1920	22.3	8.8	51.2	10.3	5.25	8.6	55/3.7	55/1.8	55/1.8	55/0.9	55/0.9	62/0.9
5/ 7	1920	21.5	8.1	40.9	8.9	3.20	8.4	56/3.7	55/1.8	55/0.9	55/0.9	55/0.9	62/0.9

-COMPLETED-

Table 20 (Continued) PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- UNOX + LIME + FILTER (UN+L+F)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
5/10	1920	22.3	8.9	17.8	6.1	3.26	8.7	50/3.7	55/1.8	55/1.8	55/0.9	55/0.9	63/0.9
5/11	1300	37.0	9.0	22.1	8.8	3.20	8.7	37/3.7	55/1.8	55/1.8	55/0.9	56/0.9	63/0.9
5/11	1900	37.0	8.8	20.0	7.5	2.88	8.6	37/3.7	55/1.8	55/1.8	55/0.9	55/0.9	63/0.9
5/12	1030	36.0	9.1	19.8	9.2	1.82	5.4	36/5.6	54/3.6	54/2.7	55/1.8	55/0.9	63/0.9
5/12	1900	37.0	9.5	18.8	9.4	1.53	5.3	37/5.9	55/3.6	55/2.7	55/1.8	55/0.9	63/0.9
5/13	1030	36.0	7.3	18.6	9.3	1.94	5.4	36/5.9	55/3.6	56/2.7	55/1.8	55/0.9	63/0.9
5/13	1900	36.5	7.0	14.8	8.6	1.60	2.9	36/3.2	55/2.3	55/1.4	55/0.9	55/0.9	63/0.9
5/14	1030	36.0	6.6	16.5	9.2	1.61	3.0	36/3.2	55/2.3	55/1.4	55/0.9	55/0.9	63/0.9
5/14	1900	37.0	6.5	13.0	10.3	1.56	2.9	37/3.2	55/2.3	55/1.4	55/0.9	55/0.9	63/0.9
5/17	1015	37.0	6.1	13.8	8.3	1.64	2.8	37/3.2	55/2.3	55/1.3	55/0.9	55/0.9	62/0.9
5/17	1900	37.0	6.4	13.8	8.0	1.39	1.7	37/1.8	56/0.9	56/0.9	55/0.9	55/0.9	63/0.9
5/18	1015	37.0	8.4	17.0	9.0	1.64	2.3	37/1.8	55/0.9	55/0.9	55/0.9	55/0.9	63/0.9
5/18	1900	37.0	8.6	15.0	7.9	1.54	2.8	37/5.1	54/1.8	55/1.3	55/0.9	55/0.9	63/0.9
5/19	800	36.5	8.6	20.0	7.3	1.38	2.8	36/5.0	55/1.8	55/1.3	55/0.9	55/0.9	59/0.9
5/19	1900	37.0	9.4	15.5	7.3	1.54	2.8	37/5.1	54/1.8	54/1.3	55/0.9	54/0.9	63/0.9
5/20	1900	38.0	8.4	14.6	8.4	1.58	3.3	38/4.9	37/1.8	37/1.3	37/0.9	37/0.9	37/0.9

-COMPLETED-

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- MINERAL CLARIFIED + CHLORINE + CARBON (MC+CL+C)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
5/21	1900	18.0	6.6	12.0	5.6	1.72	3.1	18/4.8	36/1.8	36/1.3	36/0.9	36/0.9	37/0.9
5/24	1920	20.8	7.0	11.7	4.7	1.95	2.7	36/1.8	37/0.9	37/0.9	37/0.9	37/0.9	37/0.9
5/25	930	32.0	6.4	14.8	7.1	1.90	2.8	32/1.8	37/0.9	37/0.9	37/0.9	37/0.9	37/0.9
5/25	1920	20.0	6.4	9.4	4.3	1.55	1.7	33/1.8	37/0.9	37/0.9	37/0.9	37/0.9	37/0.9
5/26	1300	20.0	5.8	9.2	4.2	1.33	1.7	20/1.8	37/0.9	37/0.9	37/0.9	37/0.9	37/0.9
5/26	1920	20.0	6.0	10.9	6.0	2.05	1.6	20/1.8	37/0.9	0/0.0	37/0.9	0/0.0	0/0.0
5/27	900	19.0	5.6	12.7	7.6	2.21	1.8	19/1.8	36/0.9	0/0.0	37/0.9	0/0.4	0/0.0
5/27	1920	19.0	5.6	13.1	7.8	2.23	1.7	19/1.8	37/0.9	0/0.0	37/0.9	0/0.4	0/0.0
5/28	900	19.5	6.0	15.2	9.8	2.49	1.8	19/1.8	36/0.9	0/0.0	37/0.9	0/0.0	0/0.0
5/28	1920	20.0	6.0	11.8	7.4	2.27	1.6	20/1.8	37/0.9	0/0.0	37/0.9	0/0.0	0/0.0
6/ 1	900	20.0	6.5	8.7	4.0	2.48	1.7	20/1.8	37/0.9	0/0.0	36/0.9	0/0.0	0/0.0
6/ 1	1920	20.0	6.9	7.0	4.3	2.46	1.7	20/1.8	37/0.9	0/0.0	37/0.9	0/0.0	0/0.0
6/ 2	200	20.0	7.0	11.7	7.4	2.26	1.6	20/1.8	37/0.9	0/0.0	37/0.9	0/0.0	0/0.0
6/ 2	900	20.0	6.6	14.3	9.5	2.05	1.7	20/1.8	36/0.9	0/0.0	36/0.9	0/0.0	0/0.0
6/ 3	830	20.0	6.1	13.7	8.5	2.06	1.7	20/1.8	37/0.9	0/0.0	37/0.9	0/0.0	0/0.0
6/ 3	1920	20.0	7.0	13.8	7.8	1.77	1.7	40/1.8	37/0.9	0/0.0	37/0.9	0/0.0	0/0.0
6/ 4	100	20.0	7.0	18.9	11.7	1.54	1.7	39/1.8	37/0.9	0/0.0	37/0.9	0/0.0	0/0.0
6/ 4	900	20.0	6.9	17.4	9.3	2.15	1.7	19/1.4	25/0.9	25/0.7	25/0.7	0/0.0	0/0.0
6/ 4	1520	20.0	6.8	18.5	9.1	1.84	1.7	19/1.4	25/0.9	25/0.7	25/0.7	0/0.0	0/0.0
6/ 7	400	20.0	6.9	10.3	5.3	2.02	1.7	20/1.4	25/0.9	25/0.7	25/0.7	0/0.0	0/0.0
6/ 7	908	20.0	6.2	11.0	6.3	2.51	1.7	20/1.4	25/0.9	25/0.6	25/0.6	0/0.0	0/0.0
6/ 7	1700	20.0	6.9	14.1	6.5	2.44	1.8	20/2.3	0/0.0	25/0.9	0/0.0	25/0.4	0/0.0
6/ 8	200	20.0	6.9	15.8	6.4	2.07	1.7	20/2.3	0/0.0	25/0.9	0/0.0	25/0.4	0/0.0
6/ 8	800	20.0	7.0	13.6	9.5	2.15	1.7	20/2.3	0/0.0	25/0.9	0/0.0	25/0.4	0/0.0

(CONTINUED)

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- MINERAL CLARIFIED + CHLORINE + CARBON (MC+CL+C)
(CONTINUED)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
6/ 9	1108	20.0	7.0	14.0	9.7	1.89	1.7	40/2.8	0/0.0	0/0.0	20/0.9	0/0.0	0/0.0
6/ 9	1700	20.0	6.2	10.8	6.8	1.75	1.6	40/2.8	0/0.0	0/0.0	20/0.9	0/0.0	0/0.0
6/10	200	20.0	5.7	14.8	7.1	1.97	1.7	39/2.8	0/0.0	0/0.0	20/0.9	0/0.0	0/0.0
6/10	945	20.0	6.0	9.3	3.5	2.22	1.7	40/2.8	0/0.0	0/0.0	20/0.9	0/0.0	0/0.0
6/10	1700	20.0	5.8	11.7	6.0	2.57	1.7	20/1.4	0/0.0	0/0.0	20/0.4	0/0.0	0/0.0
6/11	200	20.0	6.3	13.3	6.4	2.59	1.7	20/1.4	0/0.0	0/0.0	20/0.4	0/0.0	0/0.0
6/16	1600	19.0	6.0	16.9	11.4	1.79	1.7	19/1.4	30/0.4	30/0.4	30/0.4	30/0.4	30/0.4
6/17	0	20.0	6.6	14.1	10.2	1.90	1.7	20/2.3	0/0.0	25/0.9	0/0.0	24/0.4	0/0.0
6/17	1020	20.0	6.5	16.5	12.8	1.67	1.7	20/1.4	30/0.4	30/0.4	30/0.4	30/0.4	30/0.4
6/17	2000	20.0	6.3	17.7	10.5	2.54	1.7	20/1.4	0/0.0	0/0.0	20/0.4	0/0.0	0/0.0
6/18	300	20.0	6.9	16.3	10.1	2.09	1.7	0/0.0	40/2.8	0/0.0	25/0.9	0/0.0	0/0.0
6/18	930	20.0	7.1	16.4	12.6	1.88	1.7	0/0.0	40/2.8	0/0.0	25/0.9	0/0.0	0/0.0
6/18	1800	20.0	6.9	13.6	4.0	2.84	1.7	20/1.8	37/0.9	0/0.0	37/0.9	0/0.0	0/0.0
6/21	930	20.0	6.9	10.0	3.9	3.09	2.1	20/1.4	0/0.0	0/0.0	20/0.4	0/0.0	0/0.0
6/21	2100	20.0	6.6	13.2	6.0	1.73	1.7	20/1.4	30/0.4	30/0.4	30/0.4	30/0.4	30/0.4
6/22	930	20.0	6.4	17.6	13.2	2.61	1.7	20/1.4	0/0.0	0/0.0	20/0.4	0/0.0	0/0.0
6/22	1800	20.0	6.3	18.1	11.8	1.85	1.7	55/3.7	0/0.0	0/0.0	0/0.0	0/0.0	0/0.0
6/23	0	20.0	6.5	16.0	10.9	1.97	1.7	55/3.7	0/0.0	0/0.0	0/0.0	0/0.0	0/0.0
6/23	2000	20.0	7.1	19.6	9.6	4.64	6.7	54/3.7	0/0.0	0/0.0	0/0.0	0/0.0	0/0.0
6/24	130	17.0	8.5	17.6	10.8	4.21	6.7	55/3.7	0/0.0	0/0.0	0/0.0	0/0.0	0/0.0
6/24	1730	17.0	9.2	15.8	11.1	4.31	6.7	55/3.7	0/0.0	0/0.0	0/0.0	0/0.0	0/0.0
6/24	2100	17.0	8.9	18.5	12.8	1.99	2.8	17/2.7	25/0.9	25/0.9	25/0.4	25/0.4	25/0.4
6/25	200	17.0	8.2	21.8	10.4	2.38	2.8	17/2.7	25/0.9	25/0.9	25/0.4	25/0.4	25/0.4
6/25	800	18.0	9.0	16.1	8.1	2.07	2.8	17/2.7	25/0.9	25/0.9	25/0.4	25/0.4	25/0.4

(CONTINUED)

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- MINERAL CLARIFIED + CHLORINE + CARBON (MC+CL+C)
(CONTINUED)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
6/25	1500	18.0	9.1	14.3	2.6	1.77	2.8	18/2.7	25/0.9	25/0.9	25/0.4	25/0.4	25/0.4
6/28	1130	17.0	7.1	21.6	11.4	1.16	1.4	17/2.8	25/0.9	25/0.9	25/0.4	25/0.4	25/0.4
6/28	1800	17.0	5.9	15.6	11.3	1.24	1.4	17/2.7	25/0.9	25/0.9	25/0.4	25/0.4	25/0.4
6/29	230	17.0	8.4	21.2	12.1	1.52	1.4	17/2.7	25/0.9	25/0.9	25/0.4	25/0.4	25/0.4
6/29	1230	17.0	7.4	13.8	8.6	1.45	1.4	17/2.7	25/0.9	25/0.9	25/0.4	25/0.4	25/0.4
6/29	1730	17.0	7.3	15.1	7.8	1.67	1.4	0/0.0	38/2.8	35/0.9	35/0.9	35/0.4	35/0.4
6/30	1730	17.0	8.0	19.2	7.1	2.29	2.1	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 1	130	17.0	7.0	19.6	9.8	2.25	2.8	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 1	826	17.0	6.2	19.0	10.6	2.32	2.8	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 1	1630	17.0	8.7	17.3	8.4	2.41	3.1	0/0.0	40/2.7	35/0.9	35/0.9	35/0.4	35/0.4
7/ 2	100	17.0	8.1	19.8	9.7	2.59	3.1	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 2	826	17.0	6.9	18.7	11.4	2.55	3.1	0/0.0	40/2.7	35/0.9	35/0.9	35/0.4	35/0.4
7/ 2	1530	17.0	6.3	14.3	7.1	2.18	3.1	0/0.0	40/2.7	35/0.9	35/0.9	35/0.4	35/0.4
7/ 6	412	17.0	8.9	12.7	6.8	2.63	3.9	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 6	900	17.0	8.2	13.3	6.8	2.38	3.0	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 6	1700	17.0	7.1	13.3	6.8	1.95	2.5	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 6	2340	17.0	6.5	11.1	7.6	1.69	2.3	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 7	900	17.0	9.0	13.1	5.5	3.08	4.6	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 7	1900	17.0	8.1	16.5	10.6	1.73	2.1	0/0.0	40/2.8	35/0.9	35/0.9	35/0.4	35/0.4
7/ 8	1900	17.0	8.9	15.6	4.2	2.86	5.4	0/0.0	50/3.7	35/1.4	40/0.9	50/0.4	43/0.4
7/ 9	30	17.0	8.1	12.7	6.3	1.63	2.4	0/0.0	50/3.7	35/1.4	40/0.9	50/0.4	43/0.4
7/ 9	900	17.0	8.9	15.7	7.1	2.84	4.4	0/0.0	50/3.7	35/1.4	40/0.9	50/0.4	43/0.4
7/ 9	1600	17.0	6.2	15.3	6.6	1.92	2.8	0/0.0	50/3.7	35/1.4	40/0.9	50/0.4	43/0.4

-COMPLETED-

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- MINERAL CLARIFIED (MC)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
7/12	2000	32.0	8.9	49.8	20.4	2.91	6.7	55/4.6	55/4.6	55/3.6	55/2.7	55/2.7	0/0.0
7/13	200	32.0	8.0	64.4	27.5	1.97	6.7	53/4.6	55/4.6	55/3.6	55/2.7	55/2.7	0/0.0
7/13	915	32.0	7.3	55.2	24.6	1.54	4.4	55/4.1	55/4.5	55/3.6	55/2.7	55/2.7	0/0.0
7/13	1730	32.0	6.4	39.0	19.3	1.76	6.7	54/4.6	55/4.6	55/3.6	55/2.7	55/2.7	0/0.0
7/14	100	32.0	9.1	59.5	26.1	1.81	7.7	54/4.6	55/4.6	55/3.6	55/2.7	55/2.7	0/0.0
7/14	1030	32.0	8.1	44.5	15.5	2.08	7.9	54/3.2	55/4.6	55/3.6	55/2.7	55/2.7	0/0.0
7/14	1630	32.0	7.1	38.6	16.1	1.77	6.3	54/3.0	55/4.6	55/3.7	55/2.7	55/2.7	0/0.0
7/15	200	32.0	6.2	64.5	31.7	1.81	6.7	54/4.6	55/4.6	55/3.7	55/2.7	55/2.7	0/0.0
7/15	1030	32.0	8.7	50.1	21.5	1.77	6.7	52/4.1	55/4.6	55/3.6	55/2.7	55/2.7	0/0.0
7/15	1630	32.0	7.9	38.9	15.5	1.72	7.0	54/5.7	55/4.7	55/3.8	55/2.8	55/2.8	0/0.0
7/16	200	32.0	7.1	75.7	33.8	1.54	7.3	53/5.7	55/4.7	55/3.8	55/2.8	55/2.8	0/0.0
7/16	1020	32.0	6.1	49.9	21.4	1.44	5.2	52/5.7	55/4.7	55/3.8	55/2.8	55/2.8	0/0.0
7/16	1700	32.0	9.8	46.0	20.7	1.56	5.4	53/5.7	55/4.7	55/3.8	55/2.8	55/2.8	0/0.0
7/19	300	32.0	7.8	40.1	11.4	1.69	6.7	54/5.2	55/4.8	55/3.8	55/2.8	55/2.8	0/0.0
7/19	930	32.0	8.6	34.1	11.1	1.75	7.6	54/5.7	55/4.8	55/3.8	55/2.8	55/2.8	0/0.0
7/19	1700	32.0	6.0	53.9	27.5	1.72	7.7	53/5.7	53/4.7	55/3.8	55/2.8	55/2.8	0/0.0
7/20	0	20.0	9.1	55.5	21.0	1.82	7.3	48/5.7	55/4.8	55/3.8	55/2.8	55/2.8	0/0.0
7/20	1300	37.0	7.6	43.0	17.3	1.42	6.7	52/5.7	55/4.7	55/3.8	55/2.8	55/2.8	0/0.0
7/20	2000	37.0	6.0	66.0	37.6	1.62	6.7	52/5.7	55/4.7	55/3.8	55/2.8	55/2.8	0/0.0
7/21	300	20.0	10.9	61.5	23.1	1.45	6.7	48/5.7	55/4.8	55/3.8	55/2.8	55/2.8	0/0.0
7/21	1330	35.0	7.1	39.1	15.3	2.88	9.3	52/3.8	55/2.8	55/1.9	55/1.9	55/1.9	0/0.0
7/21	2000	35.0	9.8	65.3	28.6	2.66	9.1	52/6.2	55/2.8	55/1.9	55/1.9	55/1.9	0/0.0
7/22	300	20.0	8.7	67.7	22.2	2.61	9.3	46/6.2	55/2.8	55/1.9	55/1.9	55/1.9	0/0.0
7/22	1200	35.0	7.6	68.1	27.7	3.06	11.0	53/6.6	55/1.9	55/1.9	55/0.9	55/0.9	0/0.0

(CONTINUED)

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- MINERAL CLARIFIED (MC)
(CONTINUED)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
7/22	1900	35.0	7.1	72.5	41.1	3.26	10.9	53/6.7	55/1.9	55/1.9	55/0.9	55/0.9	0/0.0
7/23	300	20.0	6.1	68.9	27.7	3.08	11.0	46/6.7	55/1.9	55/1.9	55/0.9	55/0.9	0/0.0
7/23	1200	35.0	8.7	69.9	36.9	3.22	11.0	42/6.7	55/1.9	55/1.9	55/0.9	55/0.9	0/0.0
7/23	1900	41.0	7.1	52.8	19.1	3.22	11.0	42/6.7	55/1.9	55/1.9	55/0.9	55/0.9	0/0.0
7/26	1930	35.0	6.2	55.5	26.4	2.31	7.7	51/6.7	55/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/27	300	20.0	9.0	57.5	18.8	2.36	7.6	52/6.7	55/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/27	1200	35.0	9.2	42.2	17.0	2.41	7.7	53/6.7	0/0.0	50/3.8	55/1.9	55/1.9	0/0.0
7/27	1900	35.0	8.8	50.8	16.8	2.40	7.7	53/6.7	0/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/28	300	20.0	9.2	51.2	15.6	2.42	7.7	52/6.7	0/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/28	1200	35.0	8.9	42.2	17.0	2.56	7.7	53/6.7	0/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/28	1900	35.0	9.6	56.0	21.9	2.36	7.8	52/6.7	0/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/29	330	20.0	9.2	52.4	18.3	2.48	7.9	52/6.7	0/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/29	1530	35.0	8.9	48.4	19.2	2.77	11.0	52/6.7	0/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/29	2230	35.0	8.4	54.5	19.8	2.94	11.1	52/6.7	0/0.0	55/3.8	55/1.9	55/1.9	0/0.0
7/30	500	20.0	9.0	52.4	18.0	2.12	6.7	52/6.7	0/0.0	55/3.8	55/1.9	55/1.9	0/0.0

-COMPLETED-

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- UNOX (UN)

DATE	TIME	FEEDWATER GPM	FEEDWATER PH	COD, MG/L IN	COD, MG/L OUT	OZONE GENERATOR PCT	OZONE GENERATOR KW	MIXER FLOWS GPM WATER/SCFM GAS NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
8/ 2	2030	30.0	6.2	17.8	10.7	2.27	6.7	29/5.8	55/2.9	55/1.9	55/1.4	55/1.4	0/0.0
8/ 3	300	30.0	6.3	24.5	11.1	2.34	6.7	29/5.8	55/2.9	55/1.9	55/1.4	55/1.4	0/0.0
8/ 3	1045	29.0	5.5	27.2	15.5	2.18	7.0	29/5.8	55/2.9	55/1.9	55/1.4	55/1.4	0/0.0
8/ 3	2030	50.0	6.2	22.4	14.6	1.67	4.4	50/5.8	45/3.8	0/0.0	35/2.9	0/0.0	0/0.0
8/ 4	300	34.0	6.1	22.8	11.4	2.26	4.4	34/3.8	45/2.4	0/0.0	35/1.9	0/0.0	0/0.0
8/ 4	1052	50.0	5.9	29.1	18.0	1.97	4.4	50/5.7	45/3.8	0/0.0	35/2.8	0/0.0	0/0.0
8/ 4	2030	50.0	6.2	18.4	14.3	2.31	4.4	50/3.8	0/0.0	35/2.9	0/0.0	0/0.0	35/2.9
8/ 5	300	35.0	6.6	25.0	16.8	3.43	4.6	0/0.0	35/2.9	0/0.0	30/1.9	0/0.0	0/0.0
8/ 5	1110	56.0	6.5	29.0	17.7	3.19	4.4	0/0.0	35/3.8	0/0.0	35/0.9	0/0.0	35/1.9
8/ 5	1900	50.0	6.3	24.6	13.3	2.23	4.4	49/3.8	0/0.0	35/2.9	0/0.0	0/0.0	35/2.9
8/ 6	130	35.0	6.2	23.4	12.5	3.03	4.4	0/0.0	35/2.9	0/0.0	30/1.9	0/0.0	0/0.0
8/ 6	1300	56.0	5.9	23.3	15.3	1.95	4.4	0/0.0	56/3.8	0/0.0	30/0.9	0/0.0	30/1.9
8/ 6	1830	50.0	6.2	21.4	11.3	2.30	4.4	49/3.8	0/0.0	35/2.9	0/0.0	0/0.0	35/2.9
8/ 9	300	35.0	6.0	21.4	11.7	3.36	4.4	0/0.0	35/2.9	0/0.0	30/1.9	0/0.0	0/0.0
8/ 9	1200	55.0	5.8	22.9	13.2	2.56	4.4	0/0.0	55/3.8	0/0.0	55/0.9	0/0.0	35/1.9
8/ 9	1908	53.0	6.0	21.7	12.8	2.47	4.4	53/3.8	0/0.0	35/2.9	0/0.0	0/0.0	35/2.9
8/10	300	35.0	6.0	22.5	11.2	3.18	4.4	0/0.0	35/2.9	0/0.0	30/1.9	0/0.0	0/0.0
8/10	1200	54.0	5.8	22.8	13.2	2.41	4.4	0/0.0	55/3.8	0/0.0	55/0.9	0/0.0	35/1.9
8/10	1900	52.0	5.9	24.8	15.2	2.36	4.4	52/3.8	0/1.4	0/1.4	0/0.9	0/0.9	0/0.9
8/11	300	35.0	5.9	21.2	6.8	2.93	4.4	35/2.4	0/0.9	0/0.4	0/0.0	0/0.4	0/0.0
8/11	1200	54.0	5.8	27.4	13.8	2.45	4.4	0/0.0	55/3.8	0/0.9	0/0.9	0/0.9	0/0.0
8/11	1900	53.0	5.9	25.0	15.2	2.32	4.4	53/3.8	0/1.4	0/1.4	0/0.9	0/0.9	0/0.9
8/12	300	35.0	5.9	25.6	14.3	2.95	4.4	35/2.4	0/0.9	0/0.4	0/0.4	0/0.4	0/0.0
8/12	1200	54.0	5.8	22.5	15.1	2.49	4.6	0/0.0	55/3.8	0/0.9	0/0.9	0/0.9	0/0.0

(CONTINUED)

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- UNOX (UN)
(CONTINUED)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
8/13	300	35.0	5.9	23.6	10.8	3.02	4.4	34/2.4	35/0.9	35/0.4	35/0.4	35/0.4	0/0.0
8/13	1200	54.0	5.8	42.0	17.6	2.58	4.4	0/0.0	55/3.8	55/0.9	55/0.9	55/0.9	0/0.0
8/16	230	36.0	6.0	27.6	14.8	2.16	2.8	36/2.4	35/0.9	35/0.4	35/0.4	35/0.4	0/0.0
8/16	1100	54.0	6.0	32.5	18.8	1.97	2.8	0/0.0	55/3.8	55/0.9	55/0.9	55/0.9	0/0.0
8/16	2000	52.0	5.9	33.7	19.6	1.65	2.8	52/3.8	50/1.4	50/1.4	50/0.9	50/0.9	50/0.9
8/17	200	35.0	5.9	29.2	19.2	1.86	2.8	35/2.4	35/0.9	35/0.4	35/0.4	35/0.4	0/0.0
8/17	1100	54.0	6.2	34.4	17.8	2.32	3.1	0/0.0	55/2.7	55/0.4	55/0.9	55/0.9	0/0.0
8/17	1900	51.0	6.2	33.6	17.8	1.54	2.8	51/3.8	50/1.4	50/1.4	50/0.9	50/0.9	50/0.9
8/18	436	35.0	6.2	26.5	14.6	2.30	2.8	35/2.4	35/0.9	35/0.4	35/0.4	35/0.4	0/0.0
8/19	1020	54.5	6.2	38.7	15.4	2.04	2.9	0/0.0	55/3.8	55/0.9	55/0.9	55/0.9	0/0.0

-COMPLETED-

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- MINERAL CLARIFIED + CHLORINE (MC+CL)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
8/20	1238	20.0	7.3	46.4	31.2	2.22	3.9	0/0.0	0/0.0	30/3.8	35/1.9	35/1.9	35/1.4
8/20	400	20.0	7.6	48.8	28.6	2.35	3.9	0/0.0	0/0.0	35/3.4	35/1.9	35/1.4	35/0.9
8/23	1200	20.0	7.5	38.7	9.7	2.52	8.2	20/4.8	0/0.0	35/3.8	35/2.8	35/0.9	35/0.9
8/24	30	20.0	8.3	43.3	15.5	1.73	3.9	0/0.0	0/0.0	35/3.8	35/1.9	35/1.9	35/1.4
8/24	2030	35.0	7.4	55.5	34.3	2.12	6.4	35/4.8	35/2.8	35/1.9	35/1.9	35/0.9	35/0.9
8/25	330	23.0	7.5	63.0	42.2	1.95	3.9	0/0.0	0/0.0	35/3.8	35/1.9	35/1.9	35/1.4
8/25	1200	35.0	6.9	58.3	43.7	2.47	6.3	35/3.8	35/2.4	35/1.4	35/0.9	35/0.9	35/0.9
8/25	1930	35.0	6.5	43.8	32.1	2.41	6.3	35/3.8	35/2.4	35/1.4	35/0.9	35/0.9	35/0.9
8/26	330	20.0	7.6	42.2	27.2	1.76	4.1	20/3.8	35/2.4	35/1.4	35/0.9	35/0.9	35/0.9
8/26	1200	35.0	6.5	36.4	20.4	2.34	6.3	35/3.8	35/2.4	35/1.4	35/0.9	35/0.9	35/0.9
8/26	1800	35.0	7.5	36.4	25.3	2.58	6.3	35/3.8	35/2.4	35/1.4	35/0.9	35/0.9	35/0.9
8/27	130	20.0	6.0	47.5	17.8	1.65	3.6	20/4.8	35/2.4	35/1.4	35/0.9	35/0.9	35/0.9

-COMPLETED-

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- 3-STAGE BIOLOGICAL + FILTER (3B+F)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
8/27	1330	35.0	6.6	23.0	9.7	1.72	4.4	35/3.8	35/2.9	35/1.4	35/0.9	35/0.9	35/0.9
8/27	1900	35.0	6.8	17.2	8.2	1.76	4.4	35/3.8	35/2.9	35/1.4	35/0.9	35/0.9	35/0.9
8/30	1215	35.0	6.6	14.1	5.1	1.47	3.4	35/3.8	35/2.9	35/1.4	35/0.9	35/0.9	35/0.9
8/30	1930	35.0	6.8	12.5	5.1	0.86	1.7	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
8/31	300	20.0	6.6	14.0	5.1	2.47	3.0	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
8/31	745	20.0	6.8	15.2	2.8	3.56	6.7	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
8/31	2030	35.0	4.9	14.0	8.8	0.93	1.7	37/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 1	100	20.0	6.5	12.4	6.4	2.09	2.8	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/ 1	1208	20.0	5.2	13.2	6.0	2.46	6.7	20/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 1	2000	35.0	6.9	13.2	8.9	2.52	6.7	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 2	230	20.0	6.9	13.2	4.0	3.36	6.7	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/ 2	1300	35.0	7.0	12.8	7.1	1.20	1.7	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 2	2000	35.0	6.4	13.2	4.8	2.46	6.7	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 3	300	20.0	6.1	14.0	6.0	3.24	6.7	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/ 3	1230	35.0	5.8	16.2	9.3	1.06	1.7	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 3	1600	35.0	6.8	14.2	8.9	0.99	1.7	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 7	300	20.0	7.1	14.8	5.3	2.37	2.8	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/ 7	800	20.0	7.1	11.1	4.9	3.29	6.7	0/0.0	25/2.8	25/1.4	25/0.9	25/0.4	0/0.0
9/ 7	2000	35.0	5.2	14.0	9.5	1.10	1.7	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 8	300	20.0	6.5	11.1	4.1	1.63	1.7	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/ 8	750	20.0	6.2	11.3	3.5	1.45	2.8	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	25/0.0
9/ 8	2000	35.0	7.5	13.3	4.4	1.33	2.8	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/ 9	300	20.0	5.4	9.3	4.0	2.59	2.8	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/ 9	1230	35.0	6.6	13.2	6.0	1.47	2.8	35/3.8	38/1.9	38/1.4	38/0.9	38/0.9	38/0.4

(CONTINUED)

Table 20 (Continued) PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- 3-STAGE BIOLOGICAL + FILTER (3B+F)
(CONTINUED)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
9/ 9	2000	35.0	7.0	12.8	2.8	3.13	9.4	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4
9/10	300	20.0	6.3	12.4	2.4	3.65	8.4	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/10	730	20.0	6.0	14.2	2.4	3.51	8.4	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/13	400	20.0	7.4	11.0	0.8	1.59	1.7	0/0.0	25/2.9	25/1.4	25/0.9	25/0.4	0/0.0
9/13	1230	35.0	6.8	11.4	5.1	1.13	1.7	35/3.8	37/1.9	37/1.4	37/0.9	37/0.9	37/0.4

-COMPLETED-

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- D.C. PLANT SECONDARY EFFLUENT (DC2)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOW! GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
9/13	1900	35.0	6.8	92.0	48.6	1.99	4.4	35/4.7	35/4.7	35/2.8	35/1.8	35/0.9	35/0.9
9/14	400	35.0	7.1	110.8	67.6	2.45	8.5	35/4.7	35/4.7	35/2.8	35/1.8	35/0.9	35/0.9
9/14	1230	35.0	6.8	86.6	34.8	2.63	11.3	35/2.8	35/1.8	35/4.7	35/3.2	35/2.3	35/2.3
9/14	2000	35.0	6.6	62.3	41.0	2.55	11.2	35/4.7	0/0.0	35/4.7	35/3.8	35/2.8	35/2.8
9/15	300	35.0	6.9	113.3	67.2	2.55	11.1	35/4.7	0/0.0	35/4.7	35/3.8	35/2.8	35/2.8
9/15	1030	35.0	6.6	128.7	56.4	2.75	11.3	35/4.7	57/1.8	35/4.7	35/2.3	35/2.8	35/2.3
9/15	1900	35.0	6.6	121.1	62.2	2.68	11.0	35/4.7	57/1.9	35/4.7	35/2.3	35/2.8	35/2.3
9/16	500	35.0	6.6	122.8	74.0	3.81	11.3	0/0.0	0/0.0	35/2.3	35/2.0	35/4.2	35/2.1
9/16	1730	35.0	7.0	82.6	33.2	2.55	11.1	35/4.4	55/1.9	35/4.7	35/3.8	35/2.6	35/2.8
9/17	430	35.0	7.0	95.3	48.0	2.90	11.1	0/0.0	35/1.7	35/3.3	35/4.7	35/3.0	35/3.8
9/17	1730	35.0	7.3	91.3	49.4	2.79	11.0	35/3.3	50/1.8	35/4.7	35/3.7	35/2.8	35/2.8
9/20	300	20.0	6.8	113.1	69.6	2.88	11.1	20/3.7	0/0.0	20/4.7	20/4.7	20/4.7	20/4.7
9/20	1200	20.0	7.0	96.4	59.0	3.40	11.1	20/3.6	0/0.0	20/2.2	20/2.2	20/1.8	20/4.5
9/20	2000	35.0	7.1	115.4	65.1	2.81	11.3	34/3.7	0/0.0	35/4.6	35/3.7	35/3.7	35/3.7
9/21	0	35.0	7.0	149.1	75.0	2.16	4.4	35/0.9	0/0.0	35/4.7	35/4.2	35/4.2	35/4.2
9/21	1330	35.0	6.8	85.7	37.9	2.83	11.1	35/2.9	0/0.0	35/4.8	35/3.8	35/4.3	35/4.3
9/21	1900	20.0	7.1	85.9	34.0	2.91	11.3	20/1.9	45/3.8	35/3.8	35/3.8	35/2.9	35/1.9
9/21	2338	20.0	7.1	82.6	44.5	3.29	11.0	20/1.9	45/1.9	35/1.9	35/1.9	35/1.9	35/1.9
9/22	1250	20.0	7.1	67.1	27.5	3.16	11.4	20/1.9	50/1.9	35/1.9	35/1.9	35/1.9	35/1.9
9/22	1900	20.0	7.1	73.7	29.1	2.55	7.6	20/1.9	45/1.9	35/1.9	35/1.9	35/1.9	35/1.9
9/23	200	20.0	7.1	101.9	48.5	2.51	7.5	20/1.9	45/1.9	35/1.9	35/1.9	35/1.9	35/1.9

-COMPLETED-

Table 20 (Continued) - PLANT PROFILE DATA SETS

FEED WATER PRETREATMENT- D.C. PLANT SECONDARY EFFLUENT + LIME (DC2+L)

DATE	TIME	FEEDWATER		COD, MG/L		OZONE GENERATOR		MIXER FLOWS GPM WATER/SCFM GAS					
		GPM	PH	IN	OUT	PCT	KW	NO 1	NO 2	NO 3	NO 4	NO 5	NO 6
9/24	1230	20.0	7.6	71.2	34.0	2.31	7.1	20/1.9	65/1.9	25/1.9	25/1.9	25/1.9	25/1.9
9/24	1800	20.0	8.3	77.8	26.5	1.89	7.1	20/1.9	65/1.9	25/4.8	25/3.8	25/3.8	25/3.8
9/27	300	20.0	8.1	110.1	39.0	1.85	7.1	20/1.9	65/1.9	25/4.8	25/3.8	25/3.8	25/3.8
9/27	1030	20.0	7.1	58.0	24.0	1.98	7.2	20/1.9	65/1.9	25/4.8	25/3.8	25/3.8	25/3.8
9/27	2000	20.0	8.8	56.4	22.7	2.34	9.8	35/5.8	35/3.8	35/2.9	20/1.9	20/1.9	20/0.9
9/28	300	20.0	7.0	55.5	20.9	2.59	9.6	35/5.8	35/3.8	35/2.9	20/1.9	20/1.9	20/0.9
9/28	930	20.0	7.3	61.3	30.2	2.41	9.9	35/5.8	35/3.8	35/2.9	20/1.9	20/1.9	20/0.9
9/28	1900	20.0	7.1	69.5	31.1	2.49	9.8	35/5.8	35/3.9	35/2.9	20/1.9	20/1.9	20/0.9
9/29	300	20.0	8.8	71.8	24.5	2.42	9.8	35/5.8	35/3.8	35/2.9	20/1.9	20/1.9	20/0.9
9/29	900	20.0	7.3	63.9	27.0	2.51	9.8	35/5.8	35/3.8	35/2.9	20/1.9	20/1.9	20/0.9
9/29	1930	20.0	9.0	55.4	15.6	2.35	9.8	35/5.8	35/3.8	35/2.9	20/1.9	20/1.9	20/0.9
9/30	300	20.0	6.9	69.4	26.6	2.52	9.8	35/5.8	35/3.8	35/2.9	20/1.9	20/1.9	20/0.9
9/30	900	20.0	7.0	121.0	54.5	2.63	9.8	35/5.8	35/3.8	35/2.9	20/1.9	20/1.9	20/0.9

-COMPLETED-

APPENDIX 7

SIGNIFICANCE OF STANDARD DEVIATION VALUES

The parameter s and s_e is the unbiased estimate of the sample standard deviation or the sample standard error of estimate. It is a measure of the data scatter about a fitted curve. About 68% of the data should fall within $\pm$s of the fitted curve, 90% within $\pm$1.64s, and 95% within $\pm$1.96s. Throughout this report, the values of s and s_e have been calculated as follows:

$$s = [\sum_1^n (\bar{y}_i - y_i)^2/(n - n_c)]^{0.5}$$

where y_i is the experimental value of the dependent variable

$\bar{y}_i$ is the fitted value of the dependent variable

n is the number of data points fit

n_c is the number of coefficients adjusted

No corrections were made for the finiteness of n (e.g. Student's t).

The values of s_a, s_b, etc. are estimates of the standard deviation of a fitted coefficient. It is a measure of how far the fitted value of the coefficient may be from the "true" value. There is about 68% probability that the "true value" of a lies within $\pm s_a$ of the least-squares fitted value of a. It should be noted that s and s_e are generally independent of the number of points fitted, but s_a decreases with an increase in the number of points fit, being about proportional to $n^{-1/2}$.

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